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1. Herbert Bell: Atomic Number and Frequency Differences in Spectral Series.
   (Reprinted from *The Philosophical Magazine,* October, 1918.)

2. Elmer S. Imes: Measurements on the Near Infra-Red Absorption of some Diatomic Gases.
   (Reprinted from *The Astrophysical Journal,* November, 1919.)

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5. Walter F. Colby: Fine Structure of the Near Infra-Red Absorption Bands of the Halogen Acids.
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6. Arthur Whitmore Smith: John Tyndall (1820-1893).
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7. Walter F. Colby and Charles F. Meyer: On the Absorption Spectrum of Hydrogen Chloride.
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From the PHILOSOPHICAL MAGAZINE, vol. xxxvi. *October* 1918.

Atomic Number and Frequency Differences in Spectral Series. *By* HERBERT BELL.

IT is a well-known law † that in the visible spectrum the wave-number differences ν between the components of a doublet series, and the differences ν_1, ν_2 between the components of a triplet series vary from element to element in such a way that, for the same family (column of the Mendelejeff table), the ν's are roughly proportional to the squares of the atomic weights. We have, for example, in Baly's 'Spectroscopy,' p. 624, the following table ‡ where the argument is $1000\,\nu$ (or ν_1)/(atomic weight)^2 :—

Na 32·3	Mg 68·8	Al 152·8	O 14·5
K 37·8	Ca 66·1	Ga 168·6	S 17·7
Rb 32·3	Sr 51·5	In 172·1	Se 16·6
Cs 31·6	Ba 46·8	Tl 187·0	

If the law were accurate the arguments in the several columns would be constant. Perhaps the most thorough discussions from this point of view have been given by Rudorf § and Hicks ‖.

An attempt was made by Runge and Precht ¶ to show that the outstanding discrepancies in the above table, *e.g.* the case of thallium, are removed by assuming a different law. They stated that the logarithm of ν is linear in terms of the logarithms of the atomic weights. We shall have to refer to its correctness later.

Since Moseley's** discovery that the square root of the frequencies of the X-ray series is linear in terms of the atomic number, for all elements, more attention has naturally been turned to it than to atomic weight. In particular, Runge and Precht's method was modified in this direction by Ives and Stuhlman†† with a decided improvement especially in the case of potassium. Their paper contains no constants for the straight lines so that the agreement is only graphically demonstrated.

† Due to Kayser and Runge, and Rydberg.

‡ Due to Rydberg, Intern. Reports, ii. p. 217 (Paris, 1900).

§ *Zt. Phys. Chemie*, l. p. 100 (1904).

‖ See *e. g.* Phil. Trans. A. ccx. (1910), ccxii. (1912), ccxiii. (1913), ccxvii. (1917).

¶ Phil. Mag. v. p. 476 (1903).

** Phil. Mag. xxvii. p. 703 (1914).

†† Phys. Rev. v. p. 703 (1915).

In connexion with the discovery of triplet differences in the Radium spectrum, the Misses Anslow and Howell * have reinvestigated the alkaline earth column, plotting, however, against log (atomic number), not log (doublet difference), as was done in the above paper, but the logarithm of $(\nu_1+\nu_2)$. They obtain *graphically* good agreement with this law. They state also that the linearity is between alternate members of the same Mendelejeff column, a point of view which we shall have to modify.

There is reproduced below for reference a form of the atomic number table as given by Kossel †.

0.	I.	II.	III.	IV.	V.	VI.	VII	VIII.		
	H 1									
He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	Fl 9			
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17			
Ar 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35			
Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	43	Ru 44	Rh 45	Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53			
X 54	Cs 55	Ba 56	Earths	72	Ta 73	W 74	75	Os 76	Ir 77	Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	84	85			
Eman. 86	87	Ra 88	89	Th 90	91	U 92				

In the two diagrams shown herewith the square root of wave-number difference per cm. is plotted against atomic number N as abscissa. Unless otherwise stated, the data have been taken from Dunz's *Bearbeitung unserer Kentnisse von den Serien* ‡, with the result that, in general, the wave-number differences refer, not to any particular member of a series, but to the calculated limiting frequencies.

Fig. 1 shows the result for the Lithium column, the constituents having only doublet series. $\sqrt{\nu}$ is seen to be linear

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* Proc. Nat. Acad. Sciences, iii. p. 409 (1917).

† *Ann. d. Phys.* lix. p. 247 (1916).

‡ Dissertation. Tübingen, 1911.

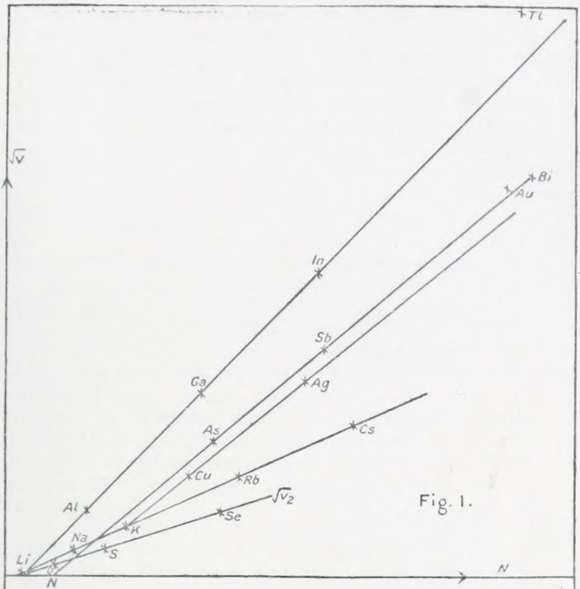
$\sqrt{v}$
Tl
Bi
Au
In
Sb
Ag
Ga
Cs
As
Cu
Rb
$\sqrt{v_2}$
Al
Se
K
Na
S
Li
N
N

Fig. 1.

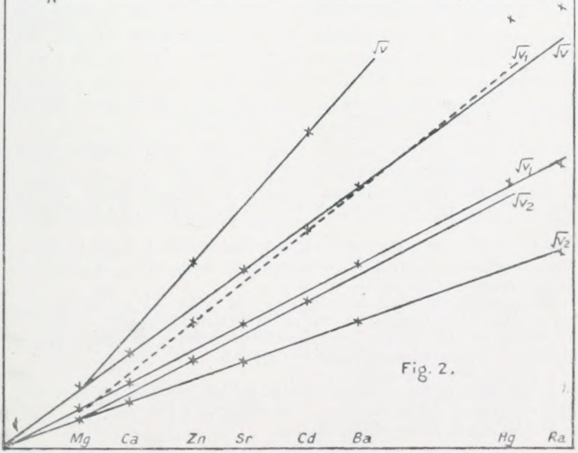
$\sqrt{v}$
$\sqrt{v_1}$
$\sqrt{v}$
$\sqrt{v_1}$
$\sqrt{v_2}$
$\sqrt{v_2}$
Mg
Ca
Zn
Sr
Cd
Ba
Hg
Ra

Fig. 2.

in *N* for Li, Na, K, Rb, Cs, although the Cs value is slightly too great. Furthermore, two other elements in the column, Cu and Ag, fall on a branch line passing through K. There is thus a *two-fold collinearity in the same vertical column of the table, one line branching off from the other just where the column itself seems to divide.* A similar feature will be met with again in the next column. Au forms an apparent exception. It is sometimes regarded as having doublets (although no series is claimed) with $\sqrt{\nu}=\sqrt{3817}$ as shown by the cross, whereas the straight line indicates $\sqrt{\nu}=\sqrt{3167}$. This point will be discussed later.

In the alkaline earth column there are both doublets and triplets (ν_1, ν_2) and the resulting collinearities are shown in fig. 2. As regards the ν-line a lower value for Mg would fit in better with Ca, Sr, and Ba. It is noticeable, from the table below, that such a modified value falls well in line with the "branch" elements Zn and Cd. For the triplet series there is a pair of straight lines for each of ν_1 and ν_2, due to branching at Mg, as the table itself suggests. In the case of ν_2 Ba has too low a value, 370 cm.$^{-1}$ instead of 401 cm.$^{-1}$, and Mg is again anomalous. A dotted line has been drawn for ν_1 as being more hypothetical; it appears to branch off for Zn and Cd to the right of Mg, and the usually accepted series for Hg give differences that lie too high [*][†].

For the next column Al, Ga, In are collinear (fig. 1), but doubt has been expressed [‡] that the doublet intervals for Ga are known. The same remark applies still more strongly to Be. $\sqrt{\nu}$ for Tl is certainly not collinear with Al and In, being 7792 cm.$^{-1}$ instead of 6323 cm^{-1}. We might plead in extenuation that the rare earths intervene in this column, but the explanation given below seems more probable. Series for Scandium [§] and Yttrium are not known.

Differences in the Carbon column are so little known that it is not possible to discuss it in this manner.

In the Nitrogen column no series have been found, but in As, Sb, and Bi Kayser and Runge [‖] discovered a new type of regularity. This consists in the recurrence of constant frequency differences between corresponding members of certain groups of lines, so that if A_r be the frequency for any line r in group A, then we have the frequency B_r in group B by adding a constant frequency β (say). Using this notation the groups for As are A_r+461, and A_r+8058. It is plain that besides the intervals 461 and 8058 there exists also $8058-461=7597$. For Sb, Kayser and Runge give $A'+2069$, $A'+8613$, $A'+9955$, $A'+12460$, and $A'+15023$, and for Bi, $A''+6225$, $A''+10245$, and $A''+21667$. By subtraction we have in Sb, 1342 and in Bi, 4020. In fig. 1 it is seen that these values, viz. 461, 1342, and 4020 for As, Sb, and Bi resp. lie on a line (very exactly as appears from the calculation below) passing nearly through a zero value for N and indicating a value 41·2 cm.$^{-1}$ for P. Examining Gautier's spectral measurements in P as quoted in Kayser's *Spektroscopie* we find the set

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[*] It is noteworthy that the interval 1545·45 cm.$^{-1}$, stated by Dunz, *loc. cit.*, as being preferred by Paschen, agrees fairly well with the value 1598 cm. required by the Zn, Cd line.

[†] The branching phenomena in these two columns is analogous to a result obtained by Rudorf, *loc. cit.* Plotting ν/A^2 against A, where A is atomic weight, he obtained *curves* for these families intersecting at these elements. There is no numerical test applied.

[‡] Kayser, *Spektroscopie*, ii. p. 547.

[§] The series in Sc suggested by Hicks, Phil. Trans. A. ccxiii. p. 408, give an interval of 320 cm.$^{-1}$; the line would give 350 cm.$^{-1}$

[‖] *Abh. Akad. Wiss. Berlin*, 1893.

4649·23 (4)	41·83	4658·29 (6r)
4575·08 (3)	41·88	4583·86 (0)
4475·43 (3r)	41·86	4483·83 (3)
4102·3 (0)	41·8	4109·34 (5)

The interval 41·8 cm. is in good agreement, but the number of cases is too small to warrant any great confidence. There are about 150 differences within the range 40 cm.$^{-1}$ to 50 cm.$^{-1}$, so that the odds against four of these falling within a given region of ·05 cm.$^{-1}$ is [*]

$$1 \div \frac{(\cdot 75)^4}{4\,!} e^{-\cdot 75} = 160.$$

Hence the odds against this group being within ·60 cm.$^{-1}$ on either side of the given line is only about 13 to 1.

In the Oxygen column triplet series occur again and the values for $\sqrt{\nu_1}$ and $\sqrt{\nu_2}$ for O, S, Se are shown in fig. 1. Collinearity exists in ν_1 but not in ν_2. For the remainder of the column we have no data.

For the halogen column, again, the data are insufficient.

In the last column frequency differences have been found by Kayser [†] for Ru, Pd, and Pt, but none in the first row Fe, Co, and Ni, so that it is not possible to apply a test.

Turning now to the first column, He, Ne, &c., there is a further possibility of linearity. Rydberg [‡] has found in

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[*] Using the formula $\frac{x}{r\,!}e^{-x}$, where x is the average density.

[†] *Abh. Berl. Akad.* 1897.

[‡] Astroph. Journal, vi. p. 239 (1897).

Argon a relationship similar to that in As, Sb, Bi, the frequencies being $A_r+846\cdot47$, $A_r+1649\cdot68$, and $A_r+2256\cdot71$. In Neon, again, according to Watson † there are triplets, one of the intervals being 417·45 cm.$^{-1}$. The line joining (1649·68, A) to (417·45, Ne) has for equation

$$\sqrt{n}=m(N-N_0)=2\cdot523(N-1\cdot90).$$

This indicates for He (N=2) the value $\nu=\cdot06$ cm.$^{-1}$ instead of about unity (Dunz gives 1·05). The line has not been drawn in the diagram; it requires for Krypton the interval 7402 cm.$^{-1}$.

The following tables contain the wave numbers whose square roots have been plotted in the diagrams. The first of the columns marked "ν calc." gives the values calculated from the equation $\sqrt{\nu}=m(N-N_0)$, m and N_0 having the values indicated. Least square methods were employed where more than two points were used to determine the line. The second "ν calc." column is calculated from $\log\nu=p\log N+q$. In each case only two pairs of values of ν and N were used to determine p and q; the results show clearly which values were chosen.

$\sqrt{\nu}=m(N-N_0)$. $\log\nu=p\log N+q$.

Doublets.

	ν obs.	ν calc.	ν calc.		ν obs.	ν calc.	ν calc.
Li ……	·34*	·25	1·03	K ……	57·90	58·1	95·2
Na ……	17·21	16·48	17·21	Cu ……	248·13	247·6	248·1
K ……	57·90	58·0	56·17	Ag ……	920·56	920·9	920·6
Rb ……	237·71	244·0	237·7	Au ……	3817·20	3172·0	3771·0
Cs ……	564·10	558·3	560·8				

$m=\cdot4447$, $N_0=1\cdot875$. $m=\cdot8117$, $N_0=9\cdot619$.
$p=2\cdot1645$, $q=-1\cdot01832$. $p=2\cdot71512$, $q=-1\cdot57591$.

Be ……		11·4	14·6				
Mg ……	92·0*	84·5	81·6	Mg ……	92·0*	85·2	113·4
Ca ……	222·9	225·5	222·9	Zn ……	872·4	872·4	872·4
Sr ……	801·3	794·7	788·2	Cd ……	2484·1	2484·1	2484·1
Ba ……	1690·5	1699·0	1690·5	Hg ……	(?)	7387·0	6904·0
Ra ……	4858·0*	4162·0	4114·0				

$m=\cdot7279$, $N_0=-\cdot630$. $m=1\cdot1280$, $N_0=3\cdot817$.
$p=1\cdot96777$, $q=-\cdot21202$. $p=2\cdot22639$, $q=-\cdot34793$.

B ……		6·14	
Al ……	112·07	112·07	112·1
Ga ……	823·6*	831·3	790·6
In ……	2212·63	2212·63	2212·6
Tl ……	7792·45*	6323·0	6859·0

$m=1\cdot0136$, $N_0=2\cdot556$.
$p=2\cdot24798$, $q=-\cdot45462$.

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† Camb. Proc. xvi. p. 130 (1911); Astroph. Journal, xxxiii. p. 399 (1911).

Triplets, ν_1, ν_2.

	ν obs.	ν calc.	ν calc.
Be		2·50	2·35
Mg	19·89	19·59	19·89
Ca	52·11	52·8	53·7
Sr	187·05	186·6	187·1
Ba	370·3*	402·2	397·6
Ra	1036·15*	987·0	957·3

$m = \cdot3552,\quad N_0 = -\cdot459.$
$p = 1\cdot94433,\quad q = -\cdot79965.$

	ν obs.	ν calc.	ν calc.
Mg	19·89	19·62	19·89
Zn	189·78	191·5	176·7
Cd	541·86	540·4	541·86
Hg	1767·19*	1598·0	1831·0

$m = \cdot5227,\quad N_0 = 5\cdot527.$
$p = 2\cdot38390,\quad q = -1\cdot37403.$

	ν obs.	ν calc.	ν calc.
Be		3·67	4·73
Mg	40·95	38·06	40·95
Ca	105·99	108·6	111·74
Sr	394·44	399·3	394·44
Ba	878·4	872·9	845·03
Ra	2016·64*	2166·3	2054·0

$m = \cdot5312,\quad N_0 = \cdot387.$
$p = 1\cdot96502,\quad q = -\cdot50836.$

	ν obs.	ν calc.	ν calc.
Mg	40·95*	27·26	45·34
Zn	388·91	388·9	388·91
Cd	1171·05	1171·0	1171·05
Hg	4630·31*	3600·0	3880·0

$m = \cdot8055,\quad N_0 = 5\cdot517.$
$p = 2\cdot34534,\quad q = -\ \cdot87450.$

	ν obs.	ν calc.
O	3·38	3·12
S	17·90	18·89
Se	103·66	103·0
Te		254·0

$m = \cdot8382,$
$N_0 = 7\cdot347.$

The ν_2 values for O, S, Se are resp. 2·76, 11·26, and 44·82 cm^{-1}.

	ν obs.	ν calc.
N		
P	41·8*	41·2
As	461·36	462·5
Sb	1342·26	1339·1
Bi	4019·73	4021·7

$m = \cdot8382,\quad N_0 = 7\cdot347.$

Values marked * are not used in determining m and N_0.

Au. The value given is criticised by Quincke, using later measurements. *Zt. f. Wiss. Phot.* xiv. p. 249 (1914).

Ba. Later measurements are by Schmitz, *Zt. Wiss. Ph.* xi. p. 209. Also by Lorenser, Dissertation, Tübingen, 1913, *Beiträge zur Kenntnis der Erdalkalien.* The latter contains a critical study of Mg, Ca, Sr, and Ba.

Hg. A detailed study of the Hg spectrum is given by Cardaun, *Zt. Wiss. Ph.* xiv. p. 89. The above values for ν_1, ν_2 are not much altered.

Sb. From later data by Schippers, *Zt. Wiss. Ph.* xi. p. 241, we have the interval 1341·17 cm. in better agreement with the straight line.

An examination of the above diagrams and tables shows, in general, an upward curvature of the observed points relative to the straight line, especially for large values of N. We notice further that, with the exception of two lines, N_0 is everywhere positive. This readily suggests that a curve passing through the origin and two of the given points might be an improvement. Runge and Precht's law mentioned above is in this direction, for, assuming $\nu = \mathrm{AN}$, where *s* and A are arbitrary, we can choose *s* nearly equal to 0·5 and the necessity for passing through the origin gives the upward curvature. The tables contain values calculated on this assumption, and it will be seen that an improvement results, especially for large values of N.

This exception is to be expected, for, if

$$\sqrt{\nu}=m(\mathrm{N}-\mathrm{N}_0)=m\mathrm{N}(1-\mathrm{N}_0/\mathrm{N})$$

be the actual locus of the given points, *i. e.*

$$\tfrac{1}{2}\log\nu=\log m+\log\mathrm{N}-\mathrm{N}_0/\mathrm{N},$$

then, on a logarithmic diagram, the points will be above the logarithmic straight line (N_0/N being negative), *i. e.* the logarithms curve downwards relatively to the actual observations. This is seen to be the case from the tables, the logarithmic set of values being worse than the others. We are therefore compelled to regard Runge and Precht's law as being of the nature of an empiricism, especially since the improvement, where it exists, is not great. The logarithmic method fails to show graphically the branching relation of the columns, as is clearly shown by a reference to the papers already cited. A further empirical improvement would plainly be effected by assuming $\nu^s=\mathrm{A}(\mathrm{N}-\mathrm{N}_0)$.

The question of doublet and triplet differences has recently been gone into extensively by Sommerfeld *. If we write the equation to a series as

$$n=\mathrm{A}\left(\frac{1}{a^2}-\frac{1}{(m+\mu)^2}\right),$$

where m has integral values and μ, a, and A are curve-fitting constants, then his theory ascribes the constant doublet differences to the term $1/a^2$. The above expression for n is in fact proportional to the loss of energy for a revolving electron when falling from an outer to an inner Bohr ring. If the inner ring for the series be in reality double (of different eccentricities according to Sommerfeld) then a has two possible values, and we have the constant frequency difference

$$\nu=n_1-n_2=\mathrm{A}\left(\frac{1}{a_1^2}-\frac{1}{(m+\mu)^2}\right)-\mathrm{A}\left(\frac{1}{a_2^2}-\frac{1}{(m+\mu)^2}\right.$$

$$=\mathrm{A}\left(\frac{1}{a_1^2}-\frac{1}{a_2^2}\right),$$

Now Moseley's equation

$$n=\mathrm{R}(\mathrm{N}-1)^2(1/1^2-1/2^2),$$

where R is Rydberg's constant and in which Sommerfeld substitutes $N-3\cdot5$ for $N-1$, gives a good account of the X-ray spectra (K_α-line). This leads us to expect that the constant A contains $(N-N_0)^2$ as a factor, where N_0 may be interpreted as the shielding effect on the outer electrons by the inner ones, the nuclear positive charge being Ne. Hence by the above equation, since u may be a constant for a given family, we might expect an equation of the form

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* *Ann. d. Phys.* li. (1916).

$$\sqrt{\nu}=m(N-N_0),$$

as is found. Against this point of view stands the fact that the limiting frequencies for the series, $\nu_\infty=A/u^2$, decrease in a given column with increasing atomic number.

In discussing the X-ray series Sommerfeld finds that the electron's increase of inertia with speed has to be taken into account. Bohr * had shown that the divergence of the observed frequencies, in the case of hydrogen, from Balmer's formula

$$n=R(1/2^2-1/m^2)$$

could be explained in this manner and corrected the formula to

$$n=R\{1/2^2-1/m^2\}\{1+\alpha^2/8(1/2^2+1/m^2)\}.$$

Here α^2 is the small quantity $(2\pi e^2/hc)^2$, (where e is the electronic charge, h Planck's constant, and c the velocity of light) occurring again as a universal constant in the discussion of the fine structure of lines. Paschen † measures it more exactly and finds, in the case of helium, that it has the value $\alpha^2=5\cdot30\times10^{-10}$ in our units. Sommerfeld ‡ develops this idea in the case of X-rays and shows, *inter alia*, that the divergence of the observed frequencies for the K and L series can also be explained in this way. If the frequencies of the K series be written

$$n=A(1/1^2-1/n^2),$$

he finds that

$$A/u^2=\left(\frac{N-k}{p}\right)^2\left[1+\frac{\alpha^2}{4}\left(\frac{N-k}{p}\right)^2+\frac{\alpha^4}{8}\left(\frac{N-k}{p}\right)^4+\;\ldots\right],$$

where $k=1\cdot6$ and $p=1$. We may therefore surmise a complete expression for $\sqrt{\nu}$ of the form

$$\sqrt{\nu}=a(N-N_0)\left[1+\eta(N-N_0)^2+\epsilon(N-N_0)^4+\;\ldots\right],$$

where η, ϵ, ... are decreasing small quantities and η is of the order of 10^{-5} or less.

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* Phil. Mag. xxix. p. 332 (1915).

† *Ann. d. Phys.* l. p. 901 (1916).

‡ *Loc. cit.*

Now it is not possible with so few points to determine such an expansion with certainty, but we can obtain an approximation as follows :—Solving the equation

$$(1) \qquad N = N_0 + q\nu^{1/2} - r\nu^{3/2}$$

for $\sqrt{\nu}$ we obtain

$$(2)$$

$$\sqrt{\nu} = \left(\frac{N-N_0}{q}\right)\left[1 + \frac{r}{q}\left(\frac{N-N_0}{q}\right)^2 + 3\left(\frac{r}{q}\right)^2\left(\frac{N-N_0}{q}\right)^4 + \ldots.\right].$$

The constants in (1) may be obtained from three points. If, for example, we take the values for Ga, In, Tl, we find that the series obtained from

$$N = \cdot 6843 + 1\cdot 07367\,\nu^{1/2} - 2\cdot 1024 \times 10^{-5}\,\nu^{3/2},$$

$$i.\,e.\ \sqrt{\nu} = N'(1 + 1\cdot 9581 \times 10^{-5} N'^2 + 1\cdot 1503 \times 10^{-9} N'^4 + \ldots.),$$

where N' has been written for $\left(\frac{N - \cdot 6843}{1\cdot 0737}\right)$, is satisfied by all three points. Substituting $N = 13$ for Al we obtain 138·5 instead of 112·07 cm. It is plainly possible to obtain an expansion of the form (2) passing through the Al point as well. What interests us is the fact that the first coefficient is of the same magnitude as Sommerfeld's calculation (10^{-5}) ascribes to the inertia effect. The exact values obtained have no particular interest at this stage, being so dependent on the particular function chosen, but a calculation shows that the same order of magnitude for r/q corrects the points for Au and Hg. It is noticeable, on the other hand, that Bi falls into line with Sb and As without this correction, but we are dealing here, perhaps, with a phenomenon of a different kind.

Summary.

The law of Rydberg, and Kayser and Runge that the square root of the doublet and triplet differences is proportional to the atomic weights, has been subjected to numerical tests, substituting, however, atomic number for atomic weight.

A similar relationship has been found among Kayser and Runge's frequency intervals in the nitrogen column, and a frequency difference of 41·8 cm.^{-1} in the phosphorus spectrum seems to fall into line. A further linearity is indicated for the helium column.

It is found that Runge and Precht's logarithmic law is not an essential improvement. The required correction is apparently necessitated on Relativity grounds.

It is shown that in two of the columns of the table there is a two-fold linearity, *the lines branching definitely at one of the elements.*

The Physical Laboratory.
The University of Michigan.
June 1918.

MEASUREMENTS ON THE NEAR INFRA-RED ABSORPTION OF SOME DIATOMIC GASES

ELMER S. IMES

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MEASUREMENTS ON THE NEAR INFRA-RED ABSORPTION OF SOME DIATOMIC GASES

By ELMER S. IMES

The importance of the study of the near infra-red absorption bands of gases is being more clearly realized the farther this study is carried. This importance arises from two main considerations. The first is the information which the absorption in this region gives with regard to the structure and mechanics of the molecule. This includes, of course, the inferences as to atomic structure, which are not only possible, but become necessary if the molecular facts are to be explained. The second is that there is found here a new application and test for the quantum theory in that it is extended to the originally excluded region of the rotational energy of molecules.

SUMMARY OF THEORY AND PREVIOUS WORK

It was Drude[1] who first announced the theory that the infra-red absorption and emission bands of the majority of substances have their origin in the vibrations of electrically charged atoms and molecules, and not in the oscillations of the electrons within the atoms. The two widely separated absorption regions usually appearing in the infra-red spectra of gases were naturally assigned, the one in the far infra-red to molecular rotation and that in the near infra-red to atomic vibrations within the molecule. N. Bjerrum[2] pointed out, however, that in all probability the shorter-wave absorption was due to a combination of the two frequencies, that of rotation and that of vibration. This observation was based on Lord Rayleigh's[3] combination principle: viz., that an oscillator which emits and absorbs at a frequency ν_o due to its oscillations alone would, when rotating about an axis perpendicular to its line of vibration with a frequency ν_r, emit and absorb at the new frequencies $\nu_o+\nu_r$ and $\nu_o-\nu_r$. The assumption of a Maxwellian distribution of rotational velocities would require that the near infra-red band consist of two broad absorption areas having maxima at $\nu_o\pm\nu_r$, where ν_r is the most probable rotational frequency, and a sharp maximum for ν_o due to molecules whose rotation frequency was zero or in a plane perpendicular to the line of sight. W. Burmeister's[1] work in this region showed the two broad areas for most of the gases investigated, but gave no sign of the sharp line corresponding to ν_o, from which it was concluded that either the dispersion used was not great enough to show it, or, at least in the case of diatomic molecules, there might be no absorption for ν_o, i.e., no molecules having no rotation.

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[1] *Annalen der Physik* (4), 14, 677, 1904.

[2] *Nernst Festschrift*, p. 90, 1912.

[3] *Philosophical Magazine* (5), 24, 410, 1892.

H. Rubens and H. von Wartenberg[2] had found in the far infra-red the bands for some of the gases investigated by Burmeister, and the values for ν_r computed from Burmeister's doublet maxima agreed well with their directly obtained values.

A complication arose, however, in the discovery that these near infra-red absorption bands did not always present, even with the low dispersion available, continuous areas with a single maximum each for $\nu_o+\nu_r$ and $\nu_o-\nu_r$. Rubens'[3] work on the water-vapor band at 6 μ and even F. Paschen's[4] much earlier work on the same band showed many separate maxima in these areas. Finally Eva von Bahr[5] in her work on water-vapor and hydrochloric acid showed such marked discontinuity in these bands that an extension[6] of the theory of their origin, abandoning the assumption of a Maxwellian distribution of rotational velocities and introducing the quantum theory, was made necessary. As a matter of fact W. Nernst[7] had previous to this time arrived at the conclusion that the quantum theory must be applied to molecular rotation. This conclusion was based on two observations: first, that molecular rotation causes radiation in the case of charged molecules; and, second, that even for infinitely thick layers of gas no shorter wave-lengths are emitted. Work was done on the specific heat of gases at low temperatures with a view to finding this quantum effect, and various explanations of the results arrived at were attempted. Perhaps the best of these was that of P. Ehrenfest[1] who proposed the equation

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[1] *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 589, 1913.

[2] *Ibid.*, 13, 796, 1911.

[3] *Sitzungsberichte Preussische Akademie*, p. 513, 1913.

[4] *Wiedemanns Annalen*, **52**, 215, 1894.

[5] *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 710, 731, 1150, 1913

[6] N. Bjerrum, *loc. cit.;* E. von Bahr, *loc. cit.;* A. Eucken, *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 1159, 1913.

[7] *Zeitschrift für Elektrochemie*, **17**, 265, 1911.

$$\tfrac{1}{2}I(2\pi\nu_r)^2 = n\frac{h\nu_r}{2},$$

(where I is the moment of inertia of the molecule, ν_r the rotation frequency, n a whole number, and h Planck's constant), as representing the energy of rotation of a diatomic molecule and as a starting point in the desired explanation. This equation differs from that proposed by Bjerrum[2] by the factor 2 in the denominator of the second member of the equation, since Ehrenfest concluded that the rotation quantum of energy is $h\nu_r/2$ instead of $h\nu_r$ as assumed by Bjerrum. E. C. Kemble[3] gives a derivation, based on the classical statistical mechanics, which leads to the equation

$$I = \frac{KT}{4\pi^2\bar{\nu}_r^2 N}$$

as giving the moment of inertia of a diatomic molecule in terms of the rotation frequency, $\bar{\nu}_r$, obtained from the Bjerrum doublet. He shows that this checks with Ehrenfest's assumption rather than with that of Bjerrum.

It is unfortunate that only the order of magnitude of numerical results computed from such formulae is possible of verification. This, however, in no sense minimizes the importance or the desirability of further and more exact work on the infra-red absorption of diatomic gases. There can be little hope of interpreting properly the results already obtained in the cases of water-vapor and CO_2, to say nothing of more complex molecules yet to be studied, until by systematic study of these simpler diatomic molecules the material for generalization is gathered.

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[1] *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 15, 451, 1913.

[2] *Loc. cit.*

[3] *Physical Review* (2), 8, 689, 1916.

In the hope of adding to the amount of such material available for theoretical work the writer undertook the study of the absorption of HCl in the near infra-red, with greater dispersion than had previously been available. Burmeister's[1] original curve for this gas showed only the doublet consisting of broad areas having maxima at 3.4 μ and 3.55 μ. Von Bahr[2] succeeded in resolving these into twelve separate maxima, of which five were on the long-wave side of the center, thus making only five pairs available for measurement. Finally J. B. Brinsmade and E. C. Kemble[3] have published, since this work was begun, a curve for HCl showing eight maxima on the long-wave side of the center of the band at 3.46 μ, as well as a partially resolved curve for the "harmonic" at 1.76 μ.

It has been possible in the present work to extend both of these; there being twelve pairs of maxima given for the band at 3.46 μ and the band at 1.76 μ being resolved over eight pairs of maxima. In addition to these curves for HCl the writer has also obtained curves for the HBr band at 3.91 μ and the HF band at 2.52 μ. For the former of these Burmeister has published a doublet having maxima at 3.84 μ and 4.01 μ. For the latter the writer has found no published work.

APPARATUS

The apparatus designed and used by W. W. Sleator[4] in his work on water-vapor was admirably adapted to this present work and was fortunately available.

The galvanometer.—The galvanometer is of the Paschen type, a modification of the Thomson four-coil astatic instrument, and was built in the department's shop. The resistance of this galvanometer as used in the present work is approximately 2 ohms and with the scale 200 cm distant and the period adjusted to 6 seconds the sensitivity is about 2.2×10^{-11} amp. per mm deflection.

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[1] *Loc. cit.*

[2] *Philosophical Magazine* (6), **28**, 71, 1914; *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 1150, 1913.

[3] *Proceedings of National Academy of Sciences*, **3**, 420, 1917.

[4] *Astrophysical Journal*, **48**, 125, 1918.

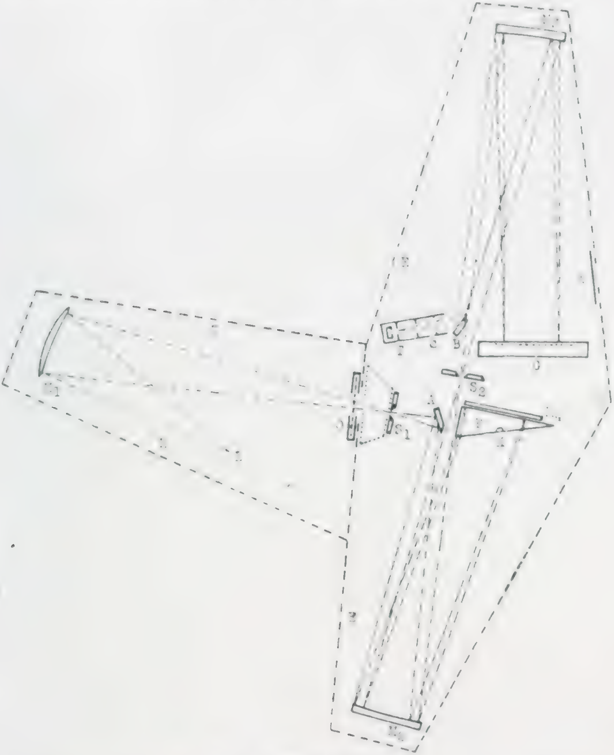

Fig. 1.—The spectrometer

L, Nernst glower; S_1, S_2, slits; M_1, 10 cm mirror, f = 30 cm; *P*, salt prism; M_2, M_3, 10 cm mirrors, f = 50 cm; M_4, *A*, *B*, plane mirrors; *G*, grating; *C*, case for *T*, the thermopile; *W*, window in box *E*; *O*, shutter. The path of the light is $LM_1S_1AM_2PM_4PM_2S_2M_3GM_1BT$. A spectrum appears at S_2. *P* and M_4 rotate together about *K*, so that any region of the spectrum may be isolated for the grating, and the overlapping of spectra is avoided. (From paper by W. W. Sleator, *Astrophysical Journal*, 48, 125, 1918.)

The spectrometer.—Figure 1 shows the arrangement of the spectrometer, which consists really of two spectrometers, both of the mirror type. The first is a prism spectrometer, $S_1AM_2PM_4M_2$, which presents a portion of its spectrum to the slit, S_2, of the grating spectrometer, $S_2M_3GM_3BT$. The prism is of rock salt and has a refracting angle of about 18°. Its face is about 12×14 cm. Three gratings were used in the course of the work—a brass grating by Hilger, a 7500-line grating, and a 20,000-line grating, both on speculum metal by Anderson, of Johns Hopkins University. With the brass grating the spectrometer constant is 211,476 A, while with the 7500-line grating it is 67,693 A and with the 20,000-line grating it is 25,375 A.

The double-spectrometer method has proved highly successful in bringing the desired high dispersion of the grating to bear on the infra-red problem. Obviously the grating must not be called upon to analyze a spectral range containing wave-lengths which are integral multiples of each other, if the results are to be interpreted. This is especially true where, as in the present case, photographs are impossible. In the double-spectrometer method a very limited portion of the prism spectrum is thrown upon the slit of the grating spectrometer. If this slit is narrow enough to allow no multiple wave-lengths to pass, the problem of overlapping is solved.

The theoretical value of the resolving power of the grating spectrometer is given in the equation

$$d\lambda/\lambda = 1/Nn$$

(where $d\lambda$ is the wave-length separation of two lines which may just be seen as separate lines, N the number of grating lines used, and n the order of the spectrum observed).

For the 7500-line grating at the center of the HCl band at 3.46 μ, the beam covering 7.5 cm of grating surface and the observations being taken in the first-order spectrum, this equation gives

$$d\lambda = \frac{3.46}{22500\times 1} = 0.00016\ \mu = 1.6\ \text{A}.$$

But this is based upon the assumption of infinitely narrow slits, which is not at all the case in this work, both slits of the grating spectrometer being 0.5 mm wide. A better idea of the resolution obtained may be gained from the following consideration. The width of the thermopile slit corresponds to 1.7 minutes' angular displacement of the grating. This is $d\theta$ in the equation

$$d\lambda = k \cos \theta d\theta$$

derived from the spectrometer equation $\lambda = k \sin \theta$. Substituting this value of $d\theta$ and that of $\cos \theta$ for $\lambda = 3.46\ \mu$, it is found that

$$d\lambda = 20.1\ \text{A}.$$

In other words the thermopile slit includes 20 A of the spectrum formed by this grating at 3.46 μ. Kemble worked with approximately 70 A and von Bahr with 100 A for their best results.

The thermopile.—The "eyepiece" of the spectrometer consists of a thermopile and the galvanometer. The thermopile is a linear bismuth-silver group made by Coblentz. It has ten junctions in its center line and a resistance of about 2 ohms. It is mounted behind a 0.5 mm slit at the focus of the mirror M_3, the beam from M_3 being reflected by the plane mirror B at about 90°, so that the thermopile will not obstruct the beam from the slit S_2 to M_3. The mounting is so designed as to keep the thermal junctions at the same temperature, except when radiation is absorbed by the row exposed to the slit.

The source.—A Nernst glower was used as the source of energy. The work was started with the Nernst lamp in practically its original form and driven by D.C. from a storage battery for the sake of steadiness. Toward the end of the work, however, the original mounting of the filament had given out and it was impossible to obtain new parts for its repair. Accordingly the expedient of simply mounting the filament in a suitable alundum cement mold and using a bank of tungsten lamps as ballast was resorted to. In order to avoid a troublesome amount of polarization of the filaments A.C. was used at this stage. As all of the observations were taken between 1:00 A.M. and 5:00 A.M., when the mechanical and magnetic disturbances to which the galvanometer responds so decidedly were at a minimum, the fluctuations of voltage on the A.C. lines were practically negligible. Furthermore, current was drawn almost directly from a transformer on the 2300-volt lines, having no other load, and the glower circuit was so arranged that the fall of potential across the filament was only a fraction of the total fall in the circuit, thus making steadiness quite assured.

The absorption chamber. The absorption chamber was of brass, 15 cm long and about 8 cm in diameter. For the greater part of the work thin mica plates were used as windows. They were cemented over the ends of the chamber, and another pair of plates, cut from the same sheets, was so mounted as to be in the beam when the chamber was out. The thickness of these plates was of the order of 0.03 mm. For work in the region of $2.5\ \mu$ and at shorter wave-lengths certain specimens of glass plates were available as windows.

Although the total length of the air path of the beam of light is more than 5 meters, the greater part of it is inside the box that contains the spectrometer, and is dried by vessels of calcium chloride, while the length of the absorption chamber is quite 20 per cent of that of the undried air path outside the box. Accordingly, for the part of the work done in regions of strong water-vapor absorption—notably at $2.6\ \mu$—it was thought best to provide a compensating chamber similar in dimensions to the absorption chamber and carefully filled with dried air that had also been freed from CO_2 by passing through KOH solution.

METHODS AND RESULTS

Hydrochloric acid.—The first work was done with HCl in the region of $3.5\ \mu$. The gas was generated by dropping H_2SO_4 on $CaCl_2$ and dried by being passed through concentrated H_2SO_4. Both chemicals were the "analyzed" product of the Baker and Adamson Company. A slow stream of the gas was kept passing through the absorption chamber and disposed of by absorption in water. Gum rubber tubing was used, since the ordinary vulcanized tubing was attacked by the HCl giving rise to enough H_2S to be distinctly perceptible by its odor. The unequivocal nature of the curves obtained is taken as sufficient evidence of the purity of the HCl thus generated, so far as the presence of any substances having overlapping absorption is concerned.

For each point of the curve—one minute of arc apart—six to eight readings of the galvanometer deflection were taken through the absorbing gas and a like number through only the compensating plates, the deflections being obtained by opening or closing the shutter in front of the slit S_1. These readings were not taken consecutively, but alternately in pairs—two with the chamber "in," then two with it "out," and so on. The percentage of absorption was computed from the two averages, the direct ratio between the "in" and "out" averages being translated into a per cent transmission, and the difference between this and 100 per cent being the per cent absorption plotted against the grating setting for that point of the curve. This method has obvious advantages over a method used by some observers who have gone over the entire band first with no absorbing medium (sometimes vacuum) in the chamber, and then with the chamber filled with the substance under observation. Any failure to reproduce a spectrometer setting must result in a corresponding error in the value so obtained. This error would be especially large in the case of a substance having, for example, the very sharp absorption maxima shown by HBr (Fig. 6).

The extreme sensitivity of the galvanometer used in this work to the slightest mechanical or magnetic disturbance is a source of regret. Many times it was not possible to obtain consistent deflections even during the favorable hours, between midnight and dawn, chosen for observation. No claim for extreme accuracy is made for the percentages obtained, but it is not likely that there is any uncertainty with regard to the location of the maxima, which have all been repeated—some as many as four or five times and never with a greater disagreement than two or three angstroms. The location of these maxima, and not their magnitude, has been the problem.

Figures 2 and 3 give the curves obtained for the HCl band at 3.46 μ with two different gratings. Table II gives the measurements and computations made from the better curve. Figure 5 gives the curve obtained for the so-called harmonic of HCl at

1.76 μ with the 20,000-line grating and Table III gives the measurements and computations from this curve.

These curves as well as those for HBr and HF (Figs. 6 and 7) have been idealized to the extent of omitting small irregularities and averaging all the percentages obtained for each point. Table I gives specimen data and Fig. 4 shows the actual curve plotted from this data for a small portion of the HCl band at 3.46 μ.

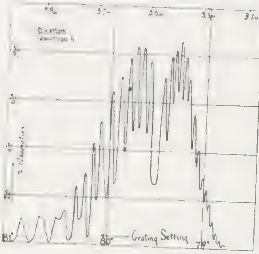

FIG. 2.—The HCl band at 3.46 μ, mapped with brass grating.

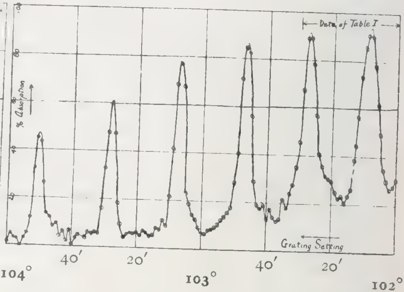

FIG. 4.—A portion of the HCl band at 3.46 μ, plotted from a single set of data.

The curves given in Figs. 2, 3, 5, 6, and 7 are plotted from averages of such sets of data and have omitted the slight irregularities appearing in the minima above, since they are not significant.

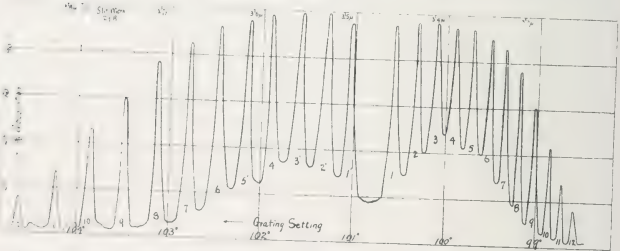

FIG. 3.—The HCl band at 3.46 μ, mapped with 7500-line grating. HCl at atmospheric pressure.

Hydrobromic acid. HBr was obtained in a satisfactorily pure state by the direct union of hydrogen and bromine. The hydrogen was obtained by the electrolysis of NaOH solution and was carefully dried. Chemically pure bromine was washed in a KOH solution and twice distilled at as low a temperature as possible. The hydrogen was then bubbled through the bromine and the mixture passed through a combustion tube in which there was a platinum coil heated to a bright red by an electric current. The product was delivered through a long vertical glass tube surrounded by a mixture of snow and calcium chloride to condense any uncombined bromine as well as any remaining traces of water-vapor. Burmeister[1] speaks of drying HBr by passing it over P_2O_5. This process would give rise to volatile compounds of phosphorus and bromine, and would no doubt account for some of the difficulty he had in obtaining satisfactorily pure HBr.

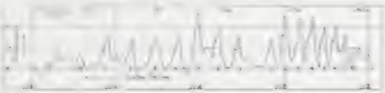

FIG. 3.—The HCl band at 1.76 μ mapped with 20,000-line grating. HCl at atmospheric pressure.

Because of the rather elaborate nature of the apparatus required for the generation of HBr no attempt was made to keep a stream of the gas passing through the absorption chamber. It was thought sufficient to start each new series of observations with a freshly generated supply, the chamber having been washed out by drawing dry air through it by means of an aspirator for half an hour before it was filled with the gas. It was difficult to determine when the pressure of the gas in the chamber was that of the atmosphere, i.e., when all the air was displaced. Furthermore, it was aimed to generate the HBr so that an excess of hydrogen would be present and no simple means of determining constancy in the amount of this excess was at hand. The result is that the relative intensities of the various absorption maxima in the curve obtained for HBr cannot be taken as significant unless they were obtained in the same series of observations. This is not important, as

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[1] *Verhandlungen der deutschen physikalischen Gesellschaft*, 15, 596, 1913.

TABLE I

Typical Data

HCl Band, 7500-line grating, June 18, 1917, 12:45 A.M.
Glower current = 0.75 amp.
Galvanometer period = 7 sec.
Grating temperature = 20°.5 C. Grating zero = 70°0'0''

Circle	In	Average	Out	Average	Percentage Trans.	Percentage Abs.
102°0'.	7.5-7.4-7.8-7.7-7.6-7.5	7.6	11.5-11-10.5-10.8-10.9-11	10.95	69.4	30.6
1'.	7.4-7.8-7.7-8.0-8.0-7.6	7.75	10.5-10.7-10.8-10.7-10.9-10.7	10.7	72.3	27.7
2'.	8.0-7.8-8.0-7.9-8.0-7.8	7.9	10.5-10.7-11-10.5-10.8-10.7	10.7	73.7	26.3
3'.	7.0-7.4-7.6-7.5-7.4-7.4	7.4	10.6-10.4-11-10.6-10.5-10.6	10.6	69.8	30.2
4'.	7.0-6.5-6.9-6.9-7.0-7.0	6.9	10.5-10.8-10.5-10.6-10.4-10.5	10.55	65.4	34.6
5'.	5.0-5.5-5.0-5.5-5.3-5.5	5.3	10.3-10.2-10.5-10.6-10.3-10.5	10.4	59.9	40.1
6'.	4.0-4.0-4.2-4.0-4.1-4.0	4.05	10.5-11-10.2-10.9-10.6-10.9	10.65	38.0	62.0
7'.	2.5-2.4-2.0-2.4-2.3-2.3	2.3	10.4-10.5-10.4-10.4-10.5-10.5	10.45	22.1	77.9
8'.	About 1.0	1.0(?)	10.6-10.5-10.7-10.7-10.6-10.5	10.6	9.4	90.6(?)
9'.	About 1.0	1.0(?)	10.3-10.3-10.8-10.2-10.3-10.5	10.4	9.6	90.4(?)
10'.	1.5-1.5-1.4-1.4-1.5-1.4	1.45	10-11-9.6-10.5-10.2-10.1	10.2	14.2	85.8
11'.	2.8-2.5-2.8-2.7-3.0-2.7	2.75	10.3-10.7-10.4-10.5-10.6-10.4	10.5	26.2	73.8
12'.	4.8-4.5-4.7-4.6-4.6-4.7	4.65	10.8-11.2-10.2-10.8-10.7-10.8	10.75	43.2	56.8
13'.	7.0-6.5-6.0-6.5-6.0-7.0	6.5	10.5-10.5-11-10.5-10.7-10.5	10.6	61.3	38.7
14'.	7.0-7.5-7.0-7.5-7.0-7.5	7.25	10.0-11-10.5-10.4-10.5-10.5	10.5	69.0	31.0
15'.	7.8-7.9-7.5-8.5-8.0-8.0	7.95	10.2-10.8-10-10.7-10.3-10.5	10.4	76.4	23.6
16'*.	11.5-11.2-11.7-11.4-11.5-11.4	11.45	14.2-15-15-14-14.5-14.6	14.55	79.2	20.8
17'.	11-11-11-10.7-11-10.8	10.9	14-14.5-14-14.2-14.1-14.3	14.2	76.7	23.3
18'.	11-10.5-11.5-11-11	11.0	14-14.2-14-14.7-14-14.3	14.2	77.5	22.5
19'.	11-10.5-11-11-11-10.9	10.9	14.7-14-15-14.2-14-15	14.5	75.2	24.8
20'.	10.5-10.5-10.5-10.2-10.3-10.5	10.4	14.6-14.8-14.7-14.9-14.7-14.8	14.75	70.5	29.5
21'.	10-10-10-10.5-10-10	10.1	14.5-14.5-14.6-14.6-14.5-14.6	14.55	69.4	30.6
22'.	10-10-10.2-10-9.8-10	10.0	14-14.9-14.6-15-14.5-14.7	14.6	68.4	31.6
23'.	9.5-9.5-9-9.5-9.5-9.5	9.4	14.9-14.2-15-14.3-14.4-14.8	14.6	64.3	35.7
24'.	8.5-8.0-9.0-8.5-8.0-9.0	8.5	14-15-14.5-14-14.2-14.7	14.4	59.0	41.0
25'.	7.0-5.0-6.0-6.0-5.5-6.5	6.0	13.8-14-14-14.2-14.1-13.9	14.0	42.8	57.2
26'.	3.0-3.0-2.8-3.0-2.9-3.0	2.95	13.8-13.8-13.7-14-13.7-13.8	13.8	21.4	78.6
27'.	1.5-1.5-1.5-1.5-1.5-1.5	1.5	14-14.5-14.3-14-14.5-14.5	14.3	10.5	89.5
28'.	1.5-1.3-1.5-1.7-1.5-1.5	1.5	14-14-14.5-13.5-14-14	14.0	10.7	89.3
29'.	4.5-4.8-4.5-4.8-4.6-4.7	4.65	14-14.5-14.5-14-14.5-14	14.25	32.6	67.4
30'.	7.5-8.0-7.5-7.0-7.5-7.5	7.5	13.5-13.8-14-13.2-13.7-13.8	13.75	54.4	45.6

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* At this point the prism was reset so as to give a greater amount of energy of the particular wave-length under study.

TABLE II

HCl Band at 3.4 μ (from curve of Fig. 3)

n	λ in μ	ν_n	$\Delta\nu_n$	ν_v	ν_v (computed)	ν_r	ν_r/n
12	3.23868	3087.68					
			[illegible]				
11	[illegible]	[illegible]					
			[illegible]				
10	[illegible]	3061.56					
			14.47				
9	[illegible]	3047.09					
			15.90				
8	[illegible]	3031.19					
			14.02				
7	[illegible]	3016.28					
			16.30				
6	[illegible]	2999.98					
			17.62				
5	[illegible]	2982.36					
			17.38				
4	[illegible]	2964.98					
			18.62				
3	[illegible]	2946.36					
			18.35				
2	[illegible]	2928.01					
			20.24				
1	[illegible]	2907.77					
			41.60				
1′	3.48897	2866.17		2886.97	2886.73	20.80	20.80
			21.75				
2′	3.51566	2844.42		2886.22	2885.83	41.79	20.89
			22.48				
3′	3.54366	2821.94		2884.15	2884.13	62.21	20.74
			22.49				
4′	3.57214	2799.45		2882.21	2882.23	82.76	20.69
			23.04				
5′	3.60178	2776.41		2879.38	2879.52	102.97	20.59
			23.85				
6′	3.63298	2752.56		2876.27	2876.22	123.71	20.62
			23.67				
7′	3.66450	2728.89		2872.58	2872.32	143.69	20.53
			25.30				
8′	3.69878	2703.59		2867.39	2867.81	163.80	20.48
			25.03				
9′	3.73335	2678.56		2862.83	2862.71	184.26	20.47
			25.91				
10′	3.76982	2652.65		2857.11	2857.03	204.45	20.45
			26.15				
11′	3.80735	2626.50		2850.69	2850.67	224.16	20.38
			26.62				
12′	3.84633	2599.88		2843.78	[illegible]	243.90	20.33

NOTE.—In this and succeeding tables and figures n refers to the number of the absorption maximum counting from the center of the band. The subscripts v and r refer to vibration and rotation, as in the "Discussion of Results." Wave-numbers are given throughout instead of actual frequencies. ν_n stands for $n_n/3\times10^{10}$.

remarked previously, since the interest has been only in the location of these maxima, and variations in pressure do not displace them laterally.

TABLE III

HCl Band at 1.76 μ (from curve of Fig. 5)

n	λ (in μ)	ν_n	$\Delta\nu_n$	ν_{on}	ν_{on} Computed	ν_{rn}	ν_{rn}/n
8	1.72711	5790.00	10.85				
7	1.73036	5779.15	12.58				
6	1.73413	5766.57	14.28				
5	1.73844	5752.29	14.18				
4	1.74274	5738.11	15.55				
3	1.74747	5722.56	16.58				
2	1.75255	5705.98	17.58				
1	1.75797	5688.40	42.03				
1′ . . .	1.77015	5646.37	23.17	5667.38	5666.38	21.01	21.01
2′	1.77835	5623.20	23.16	5664.59	5664.61	41.39	20.70
3′	1.78570	5600.04	23.70	5661.30	5661.67	61.26	20.42
4′	1.79320	5576.34	25.80	5657.22	5657.55	80.88	20.22
5′	1.80163	5550.54	25.58	5651.41	5652.25	100.87	20.17
6′	1.80997	5524.96	26.64	5645.77	5645.78	120.80	20.13
7′	1.81874	5498.32	29.71	5638.74	5638.12	140.42	20.06
8′	1.82862	5468.61		5629.31	5629.29	160.70	20.09

The 7500-line grating was used and the long-wave limit was determined by the strong atmospheric absorption beyond 4.2 μ, which cut down the galvanometer deflections to so small a figure as to magnify unduly any observational errors in computing the differential effect sought. It was possible, however, to obtain nine good maxima on the long-wave side of the center of the band. The curve is given in Fig. 6, and the table of values read and computed appears as Table IV.

A search was made for the "harmonic" of HBr at 2 μ found by Brinsmade and Kemble.[1] Nothing was found by any one of the three gratings, the conclusion being that the length of the column of absorbing gas was not great enough to give strong absorption in this region, nor was it possible in the time available to do the remodeling of the apparatus that a sensibly longer chamber would require.

TABLE IV

HBr Band at 3.9 μ (from curve of Fig. 6)

n	$\lambda_{(\text{in } \mu)}$	ν_n	$\Delta\nu_n$	ν_m	ν_m Computed	ν_d	ν_d/n
9	3.72089	2687.53	11.82				
8	3.73731	2675.71	12.96				
7	3.75552	2662.75	13.46				
6	3.77460	2649.29	13.96				
5	3.79460	2635.33	13.46				
4	3.81407	2621.87	15.17				
3	3.83626	2606.70	15.37				
2	3.85902	2591.33	15.64				
1	3.88245	2575.69	33.50				
1′	[illegible]	[illegible]	16.05	[illegible]	2558.93	16.70	16.70
2′	3.95969	2525.45	18.05	2558.39	2558.23	32.94	16.47
3′	3.98819	2507.40	18.00	2557.05	2557.08	49.65	16.55
4′	4.01704	2489.40	18.49	2555.64	2555.46	66.23	16.56
5′	4.04700	2470.91	18.69	2553.12	2553.38	82.21	16.44
6′	4.07793	2452.22	19.33	2550.76	2550.84	98.53	16.42
7′	4.11034	2432.89	19.40	2547.82	2547.74	114.93	16.42
8′	4.14338	2413.49	20.19	2544.60	2544.37	131.11	16.30
9′	4.17833	2393.30		2540.41	2540.44	147.11	16.35

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[1] *Loc. cit.*

Hydrofluoric acid. For the purposes of this study it was thought best to investigate a third gas of the halogen acid group. Of the two remaining, HF was thought the more likely to prove of theoretical value, and, aside from the difficulty of handling, easier to obtain in a pure state.

The inside of the absorption chamber was flowed with ceresin, as also was that of what tubing it was absolutely necessary to use. The gas was generated in a small iron retort by the action of concentrated H_2SO_4 on NaF. No attempt was made to dry it, but the absorption chamber was washed out with dry air before being filled with the HF, and the absence of any fuming as the gas entered the chamber was taken as evidence of the absence of sensible amounts of moisture. Because of the gradual destruction of the surface of the plates used on the ends of the absorption chamber the percentages of apparent absorption ran gradually up until, usually at the end of from thirty minutes to an hour, it was necessary to change the plates. The expedient of spreading a thin layer of oil, grease, or even wax on the inner surfaces of the plates was tried, but greatly cut down their transparency in the region under study. This was doubly undesirable because on the long-wave side of the center of the band there is the very strong water-vapor band at $2.6\,\mu$, which also cuts down the energy in spots so as to make the observational errors unduly large. It was here that a compensating chamber filled with dried air was thought of great importance. Also a new absorption chamber

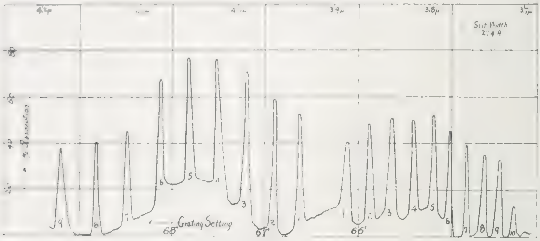

FIG. 6.—The HBr band at $3.9\,\mu$, mapped with 7500-line grating

was built, so designed that the plates could be clamped in place rather than cemented, thus saving much time in the necessarily frequent changes. Both mica and glass plates were used, those of mica proving the more satisfactory.

It is to be noted that the product of the action of HF on silica, present in both glass and mica, is a gas, SiF_4. In order to make certain that the absorption observed was not due to this second gas, observations were made at the beginning of each run with fresh plates, on one or more of the maxima previously obtained. If these had been absent or very much lowered the conclusion would have been that they were due to SiF_4 which was then present in very small quantity. No such absence or lowering was observed.

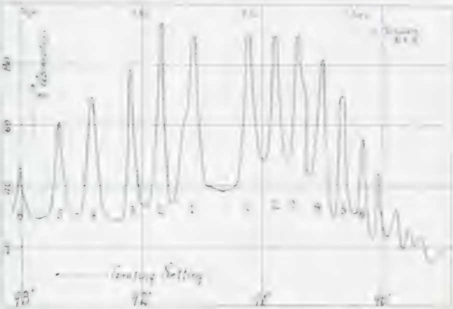

Fig. 7.—The HF band at 2.52 μ, mapped with 7500-line grating.

The long-wave limit of this work was determined by the strong atmospheric (water-vapor) absorption beyond 2.6 μ, but it is to be noted that the number of maxima on the short-wave side of the center showing strong absorption is small as compared with that observed in the case of HCl.

The 7500-line grating was used in this work, except for the preliminary exploration done with the brass grating. The curve obtained for HF is given in Fig. 7, the measurements appearing in Table V.

A preliminary search was made for the possible "harmonic," to be expected in the region of 1.25 μ, but if it exists it was effectively masked by the rising general absorption due to the action of the gas on the windows of the absorption chamber.

TABLE V

HF Band 2.5 μ (from curve of Fig. 7)

n	λ (in μ)	ν_n	$\Delta\nu_n$	ν_{on}	ν_{on} Computed	ν_{rn}	ν_{rn}/n
7.......	2.37911	4203.25					
			28.56				
6.......	2.39530	4174.69					
			31.84				
5......	2.41380	4142.85					
			32.35				
4......	2.43280	4110.50					
			34.36				
3......	2.45330	4076.14					
			36.24				
2.......	2.47531	4039.90					
			37.88				
1.......	2.49874	4002.02					
			80.17				
1′......	2.54982	3921.85		3961.93	3961.71	40.09	40.09
			42.75				
2′.....	2.57701	3879.10		3959.50	3959.43	80.40	40.20
			44.41				
3′......	2.60778	3834.69		3955.41	3955.65	120.72	40.24
			44.63				
4′.......	2.63848	3790.06		3950.28	3950.33	160.22	40.05
			46.06				
5′.......	2.67094	3744.00		3943.43	3943.49	199.42	39.88
			47.93				
6′.....	2.70557	3696.07		3935.38	3935.13	239.31	39.88

DISCUSSION OF RESULTS

Reference has been made to the variance between the assumptions of Bjerrum and of Ehrenfest with regard to the size of the quantum of rotational energy. From the newer point of view, which states more generally and precisely the postulate of stationary states, the Ehrenfest[1] equation may be justified. To do this use is made of A. Sommerfeld's[2] extension of the Planck phase-integral in which Sommerfeld splits up the general integral for f-degrees of freedom,

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[1] Proposed also by A. Eucken. See *Verhandlungen der deutschen physikalischen Gesellschaft*, **15**, 1150, 1913.

[2] *Annalen der Physik* (4), **51**, 1, 1916.

$$\int_{(f)}^{(f)} \Pi(dq_i\,dp_i) = h^f$$

(the q's are the position co-ordinates and the p's the corresponding momentum co-ordinates), into f separate integrals,

$$\int dq_i\,dp_i = h,$$

one equation for each degree of freedom. For a rotating diatomic molecule this quantum equation becomes

$$\int_0^{2\pi} I\omega_n\,d\theta = nh,$$

which must be regarded as a fundamental assumption.

In the case under consideration—that of rotation with constant angular velocity—this integral evaluates quite simply into

$$2\pi I\omega_n = nh,$$

which, written in terms of kinetic energy and rotation frequency, becomes the Ehrenfest equation,

$$\frac{1}{2}I(2\pi\nu_r)^2 = n\frac{h\nu_r}{2}.$$

From this equation there is obtained directly

$$\nu_r = n\frac{h}{4\pi^2 I}, \qquad (1)$$

giving rotation frequency in terms of the moment of inertia. This equation states that when the moment of inertia is constant, ν_r must have fixed values which are integral multiples of $h/4\pi^2 I$.

If, now, there is not the Maxwellian distribution of rotational velocities, but this series of frequencies differing by $h/4\pi^2 I$, it is evident that, still applying the combination principle, there would be expected in the near infra-red a series of pairs of absorption maxima corresponding to the frequencies $\nu_o \pm \nu_{r_n}$ grouped symmetrically about ν_o, where ν_o is, as before, the frequency of vibration of the atoms within the molecule and ν_{r_n} the rotation frequency corresponding to a given integral value of n.

Denoting the frequencies corresponding to a given pair of maxima by ν_n and $\nu_{n'}$ (the prime subscript referring to the long-wave side of the center of the band), ν_{rn} may be computed from the equations

$$\nu_n = \nu_o + \nu_{rn},$$

$$\nu_{n'} = \nu_o - \nu_{rn}, \tag{2}$$

whence

$$\nu_{rn} = \frac{\nu_n - \nu_{n'}}{2}. \tag{3}$$

The moment of inertia of the molecule will be, from equation (1),

$$I = n \frac{h}{4\pi^2 \nu_{rn}}. \tag{4}$$

From the moment of inertia thus determined it is possible to compute the length of the molecule. Assuming the masses, m_1 and m_2, of the atoms concentrated at their nuclei which are a distance l apart,

$$I = \frac{m_1 m_2}{m_1 + m_2} l^2,$$

whence

$$l = \left(I \frac{m_1 + m_2}{m_1 m_2} \right)^{\frac{1}{2}}. \tag{5}$$

For $n = 1$, i.e., for molecules having one quantum of rotational energy, the following experimental values are obtained by means of equations (4) and (5):

TABLE VI.

Molecule	$I \times 10^{40}$	$l \times 10^{8}$	$I \times 10^{40}$ (Kinetic Theory)
HF	1.37	.94	....
HCl	2.64	1.28	2.45
HBr	3.27	1.42	3.35

Von Bahr[1] gives values of I and l for the HCl molecule computed from her experimental data and the Bjerrum hypothesis, differing from the values in the foregoing table by the factor 2 in the case of I and $\sqrt{2}$ in the case of l within very close agreement.

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[1] *Philosophical Magazine* (6), **28**, 82, 1914.

Some check is desirable on any such values as these. In the present case the only one available is that furnished by the kinetic theory for the moment of inertia of a diatomic molecule in terms of its most probable rotational frequency. Accepting the equation previously given,

$$I = \frac{RT}{4\pi^2\nu_r^2 N}, \tag{6}$$

and using the values obtained by Burmeister for the doublet maxima as corresponding to the most probable frequency through the equations $\nu_m = \nu_o \pm \nu_r$, values may be obtained for the moments of inertia of HCl and HBr. (The present work, it is to be observed, furnishes no data for the determination of the most probable frequency.) Taking $R = 8.36 \times 10^7$, $N = 6.12 \times 10^{23}$, and $T = 292°$, equation (6) gives:

for HCl, $I = 2.45 \times 10^{-40}$,
for HBr, $I = 3.35 \times 10^{-40}$.

It may, indeed, be questioned whether this is a real check, but at any rate the agreement is significant.

If one turns to the curve of Fig. 4 and the accompanying table, Table II, it is at once apparent that the predicted symmetry of the maxima, i.e., the arithmetic progression expected in the frequencies of the maxima, does not exist. Instead, there is a gradual increase in frequency difference between two adjacent maxima as one goes farther into the infra-red.

Starting again with equations (2), the expression

$$\nu_o = \frac{\nu_p + \nu_q}{2} \tag{7}$$

is obtained as giving the frequency of vibration of the molecule. A value of ν_o computed from each pair of maxima appears in column 5 of the table. There are as many centers, then, as pairs of maxima, and the asymmetry of the band is the consequence of the shifting of these centers farther into the infra-red as the rotation velocity increases. In other words, it appears that the vibration frequency of the atoms in the molecule is dependent on the rotation frequency of the molecule.

Denoting the series of vibration frequencies by ν_{on}, where n in the subscript refers to the number of the pair of maxima from which the value of ν_o is computed, and plotting ν_{on} against n, the curve of Fig. 8 is obtained. Fitting it to the equation $\nu_{on} = A - Bn^2$ by the method of least squares, the agreement between observed and computed values shown in columns 5 and 6 of Table II is found. The equation of this curve is

$$\nu_{on}/3\times10^{10} = 2887.03 - 0.30n^2.$$

For ν_{oo}, the extrapolated center of the band, the value is of course A of the equation above, and the corresponding wave-length is 3.4657 μ, as against 3.475 μ obtained from the doublet maxima.

Figures 9, 10, and 11 give respectively the parabolas of centers of the HCl band at 1.76 μ, the HBr band at 3.91 μ, and the HF band at 2.52 μ. From these curves Table VII is obtained:

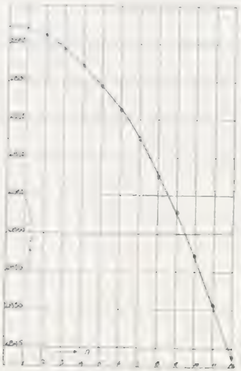

FIG. 8

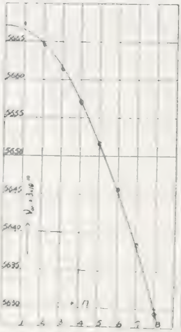

FIG. 9

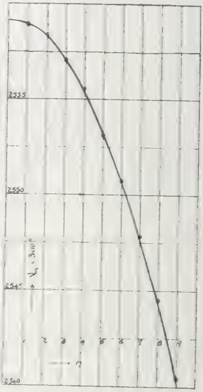

FIG. 10

FIG. 8. $\nu_{on}-n$ curve for the HCl band at 3.46 μ
FIG. 9. $\nu_{on}-n$ curve for the HCl band at 1.76 μ
FIG. 10. $\nu_{on}-n$ curve for the HBr band at 3.9 μ

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[1] See Brinsmade and Kemble, *loc. cit.*

The last column of each of Tables II to V gives the experimental values obtained for ν_{rn}/n and confirms a previous observation of von Bahr that this value is not constant but decreases with increasing values of the rotation frequency. The variation is small, but as it appears in each of the four curves it cannot be regarded as accidental. Eucken suggests that this divergence from the constancy predicted by the Bjerrum formula is not due to a falsity of the formula but to an increase of the moment of inertia with the velocity of rotation. That such an increase does take place may be seen from the following values of the moment of inertia of the HCl molecule computed from the values of ν_{rn} given in Table II.

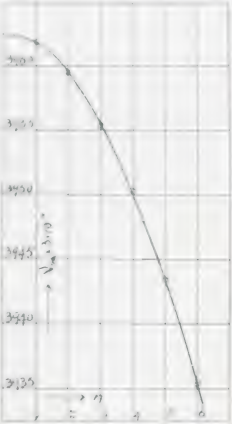

FIG. 11. $\nu_{on}-n$ curve for the HF band at 2.52μ.

The relation between I_n and n is practically linear as shown by the equation obtained from the observed values above by the method of least squares,

$$I_n = (2.593 + 0.00559n + 0.000097n^2) \times 10^{-40}.$$

The values computed from this equation (neglecting the term in n^2) are given parallel with the observed values in Table VIII.

The "harmonic."—Kemble[1] has advanced the theory that if the amplitude of vibration of the molecule be that required by even a single quantum the infra-red absorption bands discussed so far might be expected to be accompanied by faint harmonics. The center of the first harmonic according to this theory should be at one half the wave-length of the center of the fundamental and the spacing of the doublet maxima should be one fourth of that of the maxima of the fundamental doublet (in wave-length). A band approximately answering to these requirements had been observed by Burmeister in the case of carbon monoxide, and this was resolved into a doublet by Brinsmade and Kemble. They also obtained doublets for HCl and HBr approximately agreeing with the prediction. The disagreement was in the location of the centers, which were all farther in the infra-red than demanded by the theory.

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[1] *Physical Review*, 8, 701, 1916.

Figure 5 gives the curve obtained for the HCl harmonic in the present work. The extrapolated value of the frequency of the center of this band is $5666.97\times3\times10^{10}$, while that of the center of the fundamental is $2887.03\times3\times10^{10}$, the ratio being 1.963:1 instead of the expected 2:1. Or, to compare the bands as Brinsmade and Kemble compare them, the center of the harmonic is found 0.033 μ farther in the infra-red than the predicted position. This displacement is greater than the width of all eight maxima on the short-wave side of the band and greater than that observed by Brinsmade and Kemble. It disposes at once of their explanation that the disagreement observed in their work might be due to a slight error in the dispersion curve on which

TABLE VII

BAND	$\nu_{on}/3\times10^{10}$	EXTRAPOLATED CENTER	
		$\nu_{oo}/3\times10^{10}$	λ_{oo} (in μ)
HF	$3962.47-.76n^2$	3962.47	2.5237
HCl (3.46 μ)	$2887.03-.30n^2$	2887.03	3.4637
HCl (1.76 μ)	$5666.97-.59n^2$	5666.97	1.7646
HBr	$2559.16-.23n^2$	2559.16	3.9075

TABLE VIII

I_n	Observed	Computed
I_1	2.64×10^{-40}	2.636×10^{-40}
I_2	2.67×10^{-40}	2.641×10^{-40}
I_3	2.65×10^{-40}	2.647×10^{-40}
I_4	2.65×10^{-40}	2.652×10^{-40}
I_5	2.66×10^{-40}	2.658×10^{-40}
I_6	2.66×10^{-40}	2.663×10^{-40}
I_7	2.67×10^{-40}	2.668×10^{-40}
I_8	2.68×10^{-40}	2.674×10^{-40}
I_9	2.68×10^{-40}	2.680×10^{-40}
I_{10}	2.68×10^{-40}	2.685×10^{-40}
I_{11}	2.69×10^{-40}	2.690×10^{-40}
I_{12}	2.70×10^{-40}	2.696×10^{-40}

their wave-length measurements were based, since there is no uncertainty as to dispersion in the present observations, made with a grating.

It is interesting to note that the frequency differences between adjacent maxima at the centers of the two bands (fundamental and harmonic) are sensibly the same, as shown in column 4 of Tables II and III. Also the moment of inertia of the molecule computed by means of equation (4) is the same for fundamental and harmonic.

It is to be regretted that only this one harmonic was obtained, and it is to be hoped that others may be carefully measured in the near future. The apparent tendency of some of the maxima to resolve into doublets in the case of the HCl harmonic may be due to errors of observation, but it seems significant that the small secondary maxima are all on the long-wave side of the principal maxima which they accompany. It is, of course, possible that still higher dispersion applied to the problem may show even the present curves to be composite.

Accuracy.—The question of the accuracy attained in such a problem as this is of necessity quite involved. An adequate estimate, however, of the accuracy of the determinations of the positions of the absorption maxima may be obtained by reference to columns 5 and 6 of Tables II to V inclusive. Column 5 of each table gives the frequency of the centers of the various pairs of maxima of the accompanying curves from wave-length readings on the curves. Column 6 of each table gives the values for the same centers computed by the method of least squares. In the case of Table II, the greatest variation of the observed value from the computed value is in the case for $n=8$, where $d\nu = 0.42 \times 3 \times 10^{10}$. This corresponds to a value of $d\nu$ given by the equation

$$d\lambda = \frac{c}{\nu^2} d\nu$$

Substituting the values $\nu =$ [illegible] and $d\nu = 0.42 \times 3 \times 10^{10}$, it is found that

$$d\lambda = 5 \times 10^{-4} \text{ [illegible] } 5 \text{ A}$$

This is the extreme case. The average agreement is within ± 1.6 A.

SUMMARY

The object of the present work has been to obtain more extended and more accurate data with regard to the near infra-red absorption bands of certain diatomic gases than have been hitherto available. To this end the closely related HF, HCl, and HBr bands have been mapped, using greater dispersion than has been used before in this particular problem.

Curves are presented showing in greater detail the HCl bands at 1.76 μ and 3.46 μ and giving for HBr, instead of the simple doublet hitherto known, a curve resolved into its quantum lines. In addition, a similar curve is presented for HF which has not been studied before.

Several peculiarities in these curves are pointed out for the first time and one or two uncertainties in previous work are settled by material presented here.

From experimental results the lengths and moments of inertia of these three molecules have been computed.

It is hoped that in the material presented there will be found some of real value in the work which is yet to be done in reconciling theory and fact in the extremely interesting field of molecular mechanics. It is a very real pleasure to acknowledge the writer's indebtedness to Professor Randall, who suggested the problem, for his continued interest and encouragement during the progress of the work.

Physical Laboratory
University of Michigan
April [illegible], 1918

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THE OPTICAL CONSTANTS OF LIQUID ALLOYS.

BY C. V. KENT.

SYNOPSIS.

This paper describes a determination of the two optical constants of molten metals, the index of refraction, ν, and the index of absorption, κ, from the reflection of polarized light at molten-metal surfaces, placed in an inactive atmosphere.

The *purpose* of this experiment is to throw some light upon the behaviour of free electrons in metals.

Method.—The constants, ν and κ, are computed from the phase change Δ, and the azimuth change ψ, of polarized light reflected from the surface of the liquid metal at an angle of incidence ϕ. A Jamin circle is employed, the azimuth of the analyzer being determined by a bi-field of new design.

A furnace for melting the metals is made up by winding a few yards of nichrome wire on a hollow iron cone, thus maintaining a temperature of about 400° C. The whole furnace is operated in a water-cooled container through which a stream of hydrogen is made to flow continuously.

The metals employed are bismuth, cadmium, tin, lead and binary alloys of these. As a source of light, three strong rays from a quartz mercury arc are used.

Results.—A good optical surface is obtained, free from the scratches and impurities of polishing materials.

Values of $\nu^2 - \kappa^2$ and $2\nu\kappa$, are plotted as functions of the composition (atomic concentration) of each alloy. The parameters of the free electrons are also computed and plotted as functions of the composition of the alloy. These parameters are: (1) the product Ne^2/m, where the symbols have the meanings usually given in the electron theory, and (2) the frequency of impact of a free electron with the molecules of the metal.

From these optically determined free electron parameters, the electrical resistivities of the pure liquid metals and alloys are computed. In every case the agreement with the known electrical resistivity is within the limits of experimental error. A possible explanation of the disagreement between the values of resistivities for solid metals as computed from optical data and from direct electrical measurement, is suggested.

The results seem to indicate that the simple free electron theory of Drude and others is applicable to molten metals.

I. INTRODUCTION.

THE optical constants of metals (*i.e.*, the indices of refraction and absorption) are of some importance in the free electron theory. They afford a fairly direct method of obtaining a knowledge of the approximate magnitudes of some of the free electron parameters. However, the values of these optical constants as obtained experimentally for metals in the solid state, are unexpectedly unsatisfactory and inconsistent.

This is due to several causes. It is obvious that the necessary experimental data are most readily obtained by determining the changes produced in light when it is reflected from the metal to be examined; these changes being of intensity and phase. The accuracy of results is thus limited by the photometrical sensibility of the eye.

Furthermore, it is almost impossible to obtain plane surfaces which are *optically* pure, by ordinary grinding and polishing. Scratches and traces of abrasive agents, imperceptible to the naked eye, produce surfaces quite different from those of the pure metal. Minor,[1] Erochin,[2] Duncan[3] and others have minimized this source of error by using mirrors deposited on glass and examining the glass-metal inter-face. Their data show, however, that the optical constants vary with the method of producing the surfaces, whether by chemical processes, cathode deposition or casting. For these reasons, results obtained by different observers with the same metal, or even by the same observer with successive surfaces vary from 5 to 20 per cent.

The theoretical interpretation and correlation of data for different metals in the solid state is also open to objection. For example, the parameters controlling electron motion within the space lattice of a metallic crystal will be functions of direction of motion. It seems reasonable, therefore, to expect different values of the optical constants for different orientations. Thus, the optical constants of an extended solid metal surface are perhaps merely averages for the various crystals exposed.

In the course of an optical investigation of alloys, I decided to eliminate the above-named difficulties as far as possible, by restricting the work to liquid surfaces in an inactive atmosphere. By so doing, I could obtain surfaces which were perfectly smooth and practically free from contamination. Any small impurities would be either dissolved in the metal and be negligible in their effect, or, floating as solid aggregates, could be removed by mechanical means.

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[1] R. S. Minor, Ann. d. Phys., 10, 581, 1893.

[2] P. Erochin, Ann. d. Phys., 39, 213, 1912.

[3] R. W. and R. C. Duncan, PHYS. REV., 1, 294, 1913.

The investigation was further restricted to pure metals and bi-metallic alloys in which there were no compounds. In this simple case, the alloy may be considered from a theoretical point of view to consist of three mutually dissolved components: (1) The molecules of the first component metal and (2) of the second, each preserving the characteristics peculiar to the molecules of the pure metals, and (3) that portion to which metallic conduction is due. This portion is the free electrons common to all metals, and contributed in the case of the alloys here tested, by the two component metals.

II. Previous Work.

A few determinations of the optical constants of alloys have been made, most of them for the various kinds of speculum metal. Bernouilli[1] has worked with the binary mixtures Ag-Te, Ag-Sn, Cd-Hg, Cu-Sn, Cu-Zn and Cu-Ni; in each case, only a small portion of the latter component was present. Littleton[2] investigated the effect of the carbon content in various steels, and in another paper has taken up the systematic study of iron-nickel, nickel-silicon, iron-manganese, aluminum-copper, copper-nickel and iron-copper alloys. His efforts were chiefly directed to tracing the effects of the presence of compounds of the components present. Recently L. K. Oppitz[3] has studied the binary alloys of silver with copper and platinum.

Practically no results have been obtained for liquid metals with the exception of mercury. Drude mentions his apparently unsuccessful attempts to work with melted tin; he also gives some values of the optical indices for mercury alloyed with 2 per cent. tin, and for liquid Wood's metal. No other data for liquid metals has been found.

III. Method.

This is the familiar method employed in the investigation of opaque substances. Light incident upon the reflecting surface to be examined, is plane polarized in a plane at an angle of 45 degrees to the plane of incidence. The difference of phase between the two components of the reflected light is determined by a phase compensator which again plane polarizes the light passing through it. The azimuth of the plane of polarization of this light is determined by an analyzer.

Let the angle of incidence be ϕ, the phase difference introduced by reflection be Δ, and the azimuth of the plane of polarization of the reflected light with respect to the plane of incidence be ψ. In conformity with the terminology of many investigators in this subject, I have adopted the optical constants ν and κ, which are equal to Drude's *n* and *nk* respectively. The following convenient reduction formulæ may then be used to calculate ν and κ.

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[1] A. Bernouilli, Ztschr. f. Elektrochemie, 15, 647, 1909.

[2] J. T. Littleton, Phys. Rev., 28, 306, 1909; 35, 313, 1912.

[3] L. K. Oppitz, Phys. Rev., 31, 156, 1911.

$$\cos 2P = \sin 2\psi \cos \Delta, \qquad \tan Q = \tan 2\psi \sin \Delta,$$

$$S = \sin \phi \tan \phi \tan P,$$

$$\nu^2 - \kappa^2 = S^2 \cos 2Q + \sin^2 \phi = A,$$

$$2\nu\kappa = S^2 \sin 2Q = B.$$

Hence

$$2\nu^2 = \sqrt{A^2 + B^2} + A,$$

$$2\kappa^2 = \sqrt{A^2 + B^2} - A,$$

ν, κ, and the reflecting power at perpendicular incidence may then be found.

IV. Description of Apparatus.

Monochromatic Illuminator.—A Cooper-Hewitt quartz tube mercury arc was used as a source of illumination. Its light was separated into its component colors by a Wadsworth prism-mirror train. The three intense lines, 404 $\mu\mu$, 546 $\mu\mu$ and 578 $\mu\mu$ (violet, green and yellow) were used. The colored slit image of the slit in the Wadsworth train covered the collimator slit, the collimator lens being completely filled at all times with the light employed.

Spectroscope and Polarization Train.—The spectroscope was a "Cercle de Jamin" from the Société Genevoise and is evidently intended for this sort of work. As liquid surfaces were used the circle was turned into a vertical plane. The verniers of the telescope and collimator gave their position on the spectroscope circle to 30″.

The polarizer and analyzer were mounted on the objective lens end of the collimator and telescope respectively. The nicols were of the Glan-Thompson type with about 1 cm. aperture. They were perfect in action. Their divided circles could be ready by verniers to 6′.

The compensator was mounted between the polarizer and the reflecting surface. It was of the Soleil-Babinet type; the micrometer head of the screw moving the quartz wedge was divided into 100 parts, each corresponding roughly to about 1/2 degree. Thus by estimating to tenths of a division, an accuracy of about 3′ could be obtained.

The writer's experience with this compensator is identical with that of R. W. and R. G. Duncan, in that it is impossible to obtain uniform darkness over the whole field of view. With the compensator and analyzer adjusted for minimum illumination, if the telescope eyepiece was removed, the field of view presented a blotched or striated appearance. With the eyepiece in place, the collimator slit image was traversed by a dark and fairly narrow diagonal band, which shifted position very rapidly with slight changes in the compensator setting. It is probable that this defect in the action of the compensator is due to some irregularity of crystal structure in the quartz plates.

In order to use the compensator for its purpose the practice was adopted of taking all compensator readings when the center of the black band lay under the intersection of the telescope crosshairs. This was done both in the preliminary calibration of the compensator, *i.e.*, in the determination of the phase shift per division on the compensator micrometer head for each color of light used, and in the regular experimental work. In this latter work, what was measured was the phase shift necessary to bring the diagonal band back under the cross hairs when it was shifted by reflection. From the results of a number of preliminary experiments the writer is convinced that no errors were introduced by this method of using the compensator.

Bi-field.—Total extinction of the light after it was reflected could never be produced in this experimental work by any adjustments of compensator and analyzer. This was due to the following causes: the imperfection of the compensator described above; films of moisture or metal on the observation windows of the housing of the heater in which the metal was melted; sources of scattered light such as dust particles, etc., in the optical train between the nicol prisms. An azimuth bi-field was therefore absolutely necessary for determining the azimuth position of the analyzer.

An entirely new form of bi-field was invented by the writer for this purpose in 1913. It was subsequently described by Dr. F. E. Wright,[1] of the Geophysical Laboratory. As the mounting and use by the writer is quite different from the adaptation of Dr. Wright, a brief description will be given.

The bi-field (see Fig. 1) consists of two slips of glass mounted on, and rotating with the analyzer. They are situated, of course, in the beam of light from the polarizer to the analyzer. Satisfactory slips are easily cut from a good strain-free microscope slide. The slips abut along a common edge and are inclined to each other at a somewhat obtuse angle, perhaps 120 degrees. Their common edge is in (or perpendicular to) the plane of polarization of the analyzer and their faces make equal angles with the direction of the beam of light passing through them and the analyzer. The common edge is also inclined at an angle with the direction of the beam of light; the inclination is variable in order to change the sensibility of the bi-field.

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[1] F. E. Wright, Wash. J. Sci., 4, 309, 1914.

When the bi-field is in use, a short focus telescope is substituted for the eyepiece of the spectroscope telescope and focused upon the common edge of the glass slips. The field of view is thus divided in halves by this edge. The "crossed" or extinction position of the analyzer is denoted by equality of brightness of the halves of the field. The arrangement acts exactly as the usual quartz bi-field of variable sensitivity.

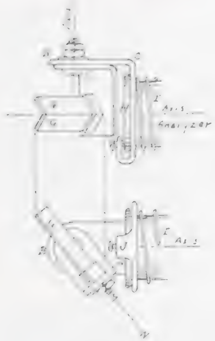

Fig. 1.

The dividing line between the halves of the field is practically eliminated (1) by mounting the glass slips with the exterior obtuse angle toward the incoming beam of light, and (2) by grinding the adjacent edges of the slips or plates to a rough fit. The interior edge of one plate is finished very sharply and overlaps the other. Thus this finely finished edge serves as a common dividing line and is practically invisible.

Multiply reflected light is present in the field of view except in a narrow band on each side of the dividing line. As the sensitivity is much reduced by this multiply reflected light, only the narrow bands are observed when obtaining the position of equal brightness.

In order to properly adjust the bi-field to the position described above it is mounted as shown in the accompanying figure. (Fig. 1).

The theory of its action is simple. Consider plane-polarized light incident upon one of the glass plates and resolve it into its two components in, and perpendicular to, the plane of incidence. By transmission these are unequally diminished with no phase difference introduced, according to the ordinary Fresnel laws. After transmission these again combine to form light of slightly diminished intensity, and on account of the inequality of diminution, plane-polarized in a slightly different plane from that of the incident light. In other words the light has been slightly diminished in intensity and *rotated through a small angle.* The light passing through the other plate will be likewise decreased in intensity and its plane of polarization also rotated, but in the opposite direction. If, now, the analyzer is in the "crossed" or total extinction position, the two glass plates are symmetrically situated, both with respect to the analyzer and the plane of polarization of the incident light.

In this case the lights passing through the two plates are equal in brightness and their planes of polarization equally rotated, but in opposite directions, with respect to the plane of polarization of the analyzing nicol. Therefore when they are observed through the analyzer the two halves of the field will be of equal brightness. When the analyzer (and glass plates) are in any other position, equality of brightness will not obtain.

The action of this bi-field is the same when it is mounted on the polarizer instead of the analyzer, and in the same position with respect to the plane of polarization of this nicol. The common edge may also be in a plane perpendicular to the plane of polarization of the nicol on which it is fastened. Owing to the mounting used, all adjustments of the bi-field for its proper action can be made optically by simple methods which need not be described here. The angle between the planes of polarization of the beams of light passing through the two plates, can be varied from 0 to about 12 degrees.

The arrangement described seems to have all the advantages of the quartz bi-field of variable sensibility. In addition its cost is insignificant and it is very easily constructed.

V. Furnace and Container.

These were mounted on a heavy laboratory tripod beside the spectroscope circle. They could be easily swung out from between the collimator and telescope at any time for adjustment, etc.

The necessary details of the heater and container for the hydrogen atmosphere above the liquid metal may be seen from the accompanying diagram (Fig. 2).

The heater, *Q*, consisted of about 8 m. of no. 28 nichrome wire imbedded in an asbestos water-glass cement. The liquid metal was held in the iron cone *Q*, whose surface was rubbed with steatite to prevent adherence. *S* is a protecting asbestos rim; an overhanging roof protects the binding posts *R*, from spilled metal. Wires from the heating coil are led outside the container through the tube *D*, in the base. The asbestos bottom of the heater is cut away over the exit tube *E* to allow for egress of detritus and samples of the metal used.

The container was made in two parts, both water-cooled. When in use these were cemented together by soft wax. The base of the container consisted of a sheet metal cylinder 12 cm. in diameter and 2 cm. high. The tubes *A* and *B* in this, are for the ingress and egress of water, *D* for the heater wires, and *E* for the dumping of detritus and samples into a beaker of water below, into which it projected. Hydrogen, which flowed slowly through the apparatus during observations, bubbled out through this tube.

The upper portion of the container was made of two concentric sheet iron cylinders soldered together at the bottom edge. The space between these was utilized for cooling water, the outer cylinder being open at the top. *F* and *G* are two short tubes to which the observation windows (two strain-free microscope slides) were fastened with soft wax. Light to and from the reflecting liquid metal surface passed through these plates practically perpendicularly. Deviations of a degree or so from this perpendicularity were found to produce no change in the analyzer settings.

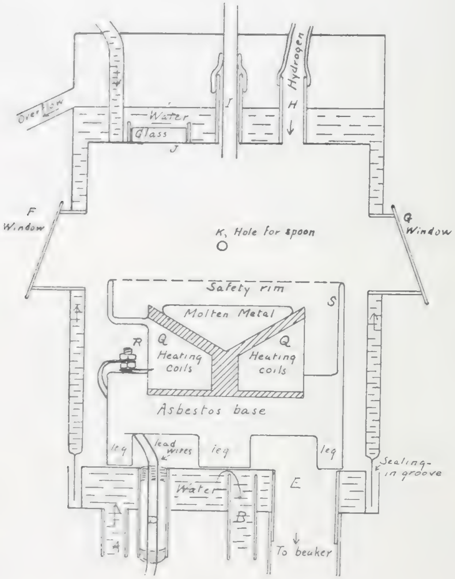

Fig. 2.

Tube *H* at the top of the container, was connected with a Kipp hydrogen generator. A glass tube slipped through tube *I*, the sliding joint being rendered gas tight by a gum rubber collar. This tube was used for the introduction of new metal when changing the composition of the alloy under observation. For this purpose it was pushed down until the lower end was immersed beneath the surface of the liquid metal. The component metal to be added was poured down through it in granular form, the tube corked and lifted up to its former position. Thus the interior of the container was at no time open to the air. *J* is an additional glass window, for the general illumination of the interior of the container, if it should be needed.

At *K*, the sides of the inner and outer container walls were pressed together and soldered, and a small hole bored through both. A short brass collar was soldered over the hole on the outside. Over this was fastened a rubber finger stall. The handle of the "skimming spoon" (to be described later) was passed through this hole into the finger stall and could be manipulated from the outside.

It was impossible to obtain a clear liquid surface when the metal was first introduced into the heater and melted. The surface was therefore freed from oxide and other coarse impurities originally present by skimming with a specially formed spoon, whose handle projected into the finger stall on the outside, as previously described. The bowl of the spoon was a sheet iron cone of practically the same shape and dimensions as the cone in which the metal was melted. A hole 1 mm. in diameter was bored at the bottom point of this cone. The stiff wire handle which passed through *K* was covered with a short piece of clay pipe stem within the finger stall. The spoon was freely movable from outside, over, and in the molten metal. It was used much like the old fashioned cream skimmer; when it was dipped into the metal and raised, the clean metal ran back through the hole, leaving the gross impurities in the spoon; these were then dumped down the exit tube *E*.

VI. Preliminary Adjustment of the Optical System.

The ordinary adjustments of the spectroscope need no description. It should be stated, however, that as the horizontal plane of the liquid reflecting surface was fixed, the optic axis of the spectroscope circle had to be brought into coincidence with it, by means of the leveling screws on the base of the instrument.

Orientation of the Plane of the Polarizer.—The ordinary means of finding this by means of reflection from a plane glass surface was found to be too inaccurate. A method was therefore devised which was quite satisfactory and is believed to be new. The compensator was removed from the instrument and the light from the polarizer, reflected from a clean pool of mercury (or other good metal surface), was examined by the analyzer. Both nicols were rotated alternately until total extinction was secured. In this case, the light coming from the metal mirror to the analyzer must have been plane polarized. Metal surfaces, however, always produce a difference of phase between the components of the reflected light in, and perpendicular to, the plane of polarization. It is evident therefore that one of these must have been absent in the reflected and also the incident light. It is therefore also evident that the planes of polarization of the two nicols must likewise be in and perpendicular respectively to the plane of incidence of the light. In which of the two planes the light from the polarizer is polarized, can be easily determined if necessary by various simple methods which need not be discussed here.

Successive positions of the polarizer as obtained by this method always agreed within the least count of the polarizer circle, *i.e.*, 6′.

The zero phase difference readings of the compensator were found to be very slightly different for the three colors used. This instrument was also found to possess a small temperature coefficient which was negligible, however, in comparison with other sources of error.

Adjustment of Bi-Field.—This is entirely optical. With the compensator removed, the analyzer and polarizer were "crossed." The common edge of the bi-plate was set approximately perpendicular to the axis of the beam of light and the bi-plane turned until its faces made *unequal* angles with the beam. The whole bi-plate mounting was then rotated on the cap of the nicol holder until total extinction of the beam was produced *through* the plates. It should be stated, that for this work the short focus telescope previously mentioned, was used as eyepiece. The common edge now lay in the plane of polarization of the analyzer, and the mounting was therefore clamped to the cap. Next, the common edge being inclined 10° to 20° to the direction of the beam of light, the bi-plate was rotated around this edge until the intensity of the halves of the field was the same. The plates now made equal angles with the beam of light, and the bi-plate bolt was clamped to the arm on which it was supported.

VII. Experimental Procedure and Calculations.

Preparing the Surface.—After the metal had been placed in the heater and the container sealed over it, hydrogen was run through the apparatus gently for about half an hour to wash out the air. The circulation of the cooling water was then started and the furnace current turned on. As no change of the optical constants of the metals with temperature could be detected, the temperature was merely kept well above the melting point, at about 400° C.

After the first fusion, the metal was cleared of dross with the skimming spoon. Traces of oxygen from the surrounding atmosphere or surfaces in the container, seemed to act on the newly skimmed surfaces until completely exhausted. When the surface was quite clean it became extremely mobile with minute pieces of oxide floating here and there. At this stage the container was swung into place beside the spectroscope circle and raised to the proper height, and the compensator and analyzer were roughly adjusted for minimum intensity of illumination. The surface was then examined without the telescope eyepiece. Surface impurities showed prominently as bright flecks or long streaks and were removed as far as possible by skimming. Those ultimately remaining usually travelled to the convex edge of the liquid as previously noted by Bidwell with similar surfaces. At the higher temperatures, actual reduction of the final oxide particles seemed to take place.

Readings.—These usually agreed within the limits of experimental error when made upon freshly cleaned surfaces. The surfaces of many alloys showed a progressive decrease of phase when left standing, although the analyzer readings were practically unaffected. It was therefore desirable to take the readings as rapidly as possible and the following order of taking observations was accordingly adopted:

1. The polarizer was set with its plane of polarization at 45° with the plane of incidence. Using the short focus telescope and bi-field, the analyzer was then accurately "crossed" with the reflected beam of light. Using the regular telescope eyepiece, the compensator was adjusted until the dark band in the slit image lay under the telescope cross hairs. Ten such compensator readings were taken for each of the three colors used.

2. The polarizer was turned through 90° and the compensator readings of 1 above repeated.

3. Using the bi-field and the short focus telescope as an eyepiece, five readings of the analyzer for a photometrically balanced field, for each of the three colors used, were taken.

4. The polarizer was turned back through 90° and 3 repeated.

5. 1 was repeated with yellow light to test possible change in the surface.

Owing to the perfection of the nicols and their divided circles it was found to be unnecessary to turn either polarizer or analyzer to positions approximately 180° from those already used. For positions of the polarizer 90° apart, the mean compensator readings were found to be consistently different by an amount varying from a few tenths to about 1° of phase difference. The cause of this consistent difference is unknown, but undoubtedly lies in the imperfections of the compensator.

Calculation of Optical Constants.—Mean values were taken in all calculations. The determinations of the angle of incidence and the phase difference indicated by the compensator are sufficiently obvious. The difference between the two mean analyzer positions for the two polarizer azimuths of 3 and 4 above was taken as 2ψ. It may have been the complement of 2ψ but as the substitution of this complement in the reduction formula used to calculate the optical constants merely produced a change of sign in the values of these constants, this uncertainty gave no trouble. For metals, $\nu^2 - \kappa^2$ is always negative, and $2\nu\kappa$ positive. The reflecting power at perpendicular incidence was calculated from the formula[1]

$$R = \frac{\nu^2 + \kappa^2 + 1 - 2\nu}{\nu^2 + \kappa^2 + 1 + 2\nu}.$$

VIII. RESULTS.

The alloys used were bismuth-lead, cadmium-lead, tin-lead and bismuth-mercury. The metals were obtained from the chemical laboratory and were pure.

1. *Bismuth-lead.*—These were very satisfactory from an optical standpoint. After skimming well, the alloy surfaces remained clean indefinitely, as the hydrogen atmosphere seemed to reduce any oxide flecks remaining.

2. *Cadmium-lead.*—The cadmium evaporated quite freely from these alloys and formed bright mirrors on the observation windows in the course of an hour or so. The depolarizing effect of the films made the compensator band faint and hazy and gave the field of the bi-plate a mottled appearance, but very good readings could be taken when the mirrors were so opaque that no details of the alloy surfaces could be seen.

3. *Tin-lead.*—Work with these alloys was extremely difficult. A few seconds after the formation of a new and clean surface, fine lines of what seemed to be minute bubbles appeared and spread until the whole surface was covered with a viscous scum, probably oxide. This formation was never entirely prevented, even when the atmosphere was practically pure hydrogen. It is probably due to oxygen originally in solution in the tin. On this account, the surface of the pure tin (or of alloys rich in this component) was renewed after every two or three readings. These readings were reproducible and the phase difference indicated by the compensator was a maximum.

4. *Bismuth-mercury.*—The accuracy of results with these alloys is relatively poor. This is due to the condensation of mercury on the observation windows, and the low temperatures necessarily employed, which prevented any reducing effect by the hydrogen.

Composition of the Alloys.—As an accuracy of more than one per cent. was not necessary, simple gravimetric determinations of the composition were made. The samples obtained from each alloy were dissolved in nitric acid. Lead was estimated as sulphate in each case, bismuth as tetroxide, cadmium as nitrate, and tin as oxide. No chemical analysis of the bismuth-mercury alloy was made. In the following tables the alloys will be defined by the atomic per cent. of one component.

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[1] Houston, A Treatise on Light, p. 417.

Tables.—The experimentally determined values of the angle of incidence ϕ, twice the azimuth angle of the reflected light (2ψ), and the phase difference, Δ, are given for each of the alloys examined. From these are calculated the optical constants $\nu^2-\kappa^2$, $2\nu\kappa$, ν, κ and R the reflecting power at perpendicular incidence.

Table I.

Bismuth-lead Alloys.

Alloy.		ϕ.	2ψ.	Δ.	$\nu^2-\kappa^2$.	$2\nu\kappa$.	ν.	κ.	Refl. Power, Per Cent.
				579μμ.					
Bismuth (pure)	A	70° 32′	63° 47′	125° 48′	9.64	20.27			
	A	70° 36′	63° 37′	124° 41′	9.36	19.47			
	B	70° 35′	64° 3′	124° 41′	9.77	19.72			
Mean values............					9.62	19.72	2.48	3.97	64.4
6 per cent. lead	C	70° 35′	64° 36′	126° 9′	10.52	20.53			
	D	70° 35′	63° 58′	124° 38′	9.69	19.40			
Mean values					10.10	19.97	2.52	4.00	64.5
19 per cent. lead....	E	70° 33′	64° 6′	124° 44′	9.79	19.37			
	F	70° 33′	64° 30′	126° 50′	10.51	21.06			
Mean values					10.15	20.21	2.48	4.03	65.0
26.4 per cent. lead . .	I	70° 33′	65° 11′	126° 23′	11.08	20.52	2.57	4.09	65.2
48 per cent. lead.	J	70° 33′	65° 16′	126° 14′	11.64	21.24			
	K	70° 33′	65° 36′	127° 17′	11.67	21.22			
Mean values					11.66	21.23	2.56	4.20	65.7
60 per cent. lead....	M	70° 33′	66° 14′	127° 1′	12.24	20.85			
	N	70° 33′	65° 54′	128° 17′	12.19	22.10			
Mean values ..					12.22	21.47	2.55	4.26	66.8
75 per cent. lead....	O	70° 33′	67° 28′	128° 48′	14.03	22.17			
	P	70° 33′	67° 12′	128° 14′	13.58	21.70			
Mean values					13.81	21.94	2.62	4.37	67.4
80 per cent. lead	Q	70° 33′	67° 23′	128° 53′	13.96	22.26	2.50	4.48	69.0
Lead (pure)........	R	70° 37′	67° 46′	129° 17′	14.63	22.74			
	S	70° 36′	68° 10′	129° 17′	15.04	22.48			
Mean values					14.84	22.61	2.56	4.53	69.2

Alloy.		ϕ.	2ψ.	Δ.	$-(\nu^2-\kappa^2)$.	$2\nu\kappa$.	ν.	κ.	Refl. Power Per Cent.
$546\mu\mu$.									
Bismuth (pure)	A	70° 32′	63° 53′	123° 36′	9.39	18.51			
	A	70° 36′	63° 47′	123° 14′	9.25	18.26			
	B	70° 35′	63° 43′	121° 56′	8.96	17.34			
Mean values					9.20	18.04	2.35	3.84	63.8
6 per cent. lead.....	C	70° 35′	64° 3′	123° 41′	9.54	18.53			
	D	70° 35′	64° 4′	122° 46′	9.39	17.87			
Mean values					9.47	18.20	2.35	3.87	64.1
19 per cent. lead....	E	70° 33′	64° 2′	123° 8′	9.42	18.13	2.35	3.86	64.1
26.4 per cent. lead..	H	70° 33′	65°	125° 58′	10.80	20.17			
	I	70° 33′	65° 9′	125° 46′	10.90	19.97			
Mean values					10.85	20.07	2.44	4.10	65.9
48 per cent. lead....	J	70° 33′	65° 26′	124° 4′	10.78	18.54			
	K	70° 33′	65° 42′	122° 2′	10.51	16.94			
Mean values					10.65	17.74	2.24	3.96	65.2
61 per cent. lead....	L	70° 33′	66° 28′	124° 14′	11.69	18.36			
	M	70° 33′	66° 25′	126° 6′	12.13	19.97			
	N	70° 33′	66° 12′	126° 24′	12.05	20.25			
Mean values					11.96	19.53	2.34	4.18	67.3
75 per cent. lead ...	O	70° 33′	67° 29′	126° 24′	13.30	19.94			
	P	70° 33′	66° 56′	126° 0′	12.66	19.73			
Mean values.......					12.98	19.84	2.32	4.28	68.4
86 per cent. lead....	Q	70° 33′	67° 40′	127° 0′	13.65	20.33	2.33	4.37	66.1
Lead (pure)........	R	70° 36′	68° 18′	127° 29′	14.57	20.71			
	S	70° 37′	68° 18′	127° 23′	14.56	20.65			
Mean values.......					14.56	20.68	2.42	4.46	69.5
$404\mu\mu$.									
Bi Pure..............	A	70° 32′	63° 43′	111° 48′	7.06	11.80	1.80	3.23	60.6
6 per cent. lead....	D	70° 35′	62° 50′	110° 54′	6.62	11.66	1.85	3.15	69.0
18 per cent. lead....	E	70° 33′	63° 49′	111° 54′	7.09	11.77	1.82	3.23	60.3
26.4 per cent. lead.	I	70° 33′	65° 24′	111° 54′	7.85	11.40	1.73	3.29	62.1
48 per cent. lead...	J	70° 33′	66° 1′	112° 24′	8.31	11.52			
	K	70° 33′	66° 13′	113° 54′	8.79	12.15			
Mean values					8.55	11.84	1.74	3.40	63.5

Alloy.		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Refl. Power, Per Cent.
[illegible]									
61 per cent. lead....	L	70° 33′	66° 56′	112° 36′	[illegible]	[illegible]			
	M	[illegible]	[illegible]	114° 6′	9.08	12.11			
	N	[illegible]	[illegible]	[illegible]	8.57	12.61			
Mean values.......					[illegible]	12.02	[illegible]	3.45	64.0
75 per cent. lead....	O	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			
	P	70° 33′	67° 40′	114° 48′	9.78	12.15			
Mean values.......					9.28	[illegible]	1.78	[illegible]	64.6
86 per cent. lead....	Q	70° 33′	68° 30′	115° 6′	10.30	12.01	1.66	[illegible]	[illegible]
Pure lead........	R	70° 36′	69° 6′	116° 18′	[illegible]	[illegible]			
	S	70° 37′	69° 54′	115° 34′	11.23	11.74			
Mean values.......					11.17	12.11	1.63	3.72	68.5

TABLE II.

Cadmium-lead Alloys.

Alloy.		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Refl. Power, Per Cent.
[illegible]									
Cadmium (pure)	A	70° 37′	82° 38′	126° 36′	25.66	8.78			
	B	70° 37′	83° 56′	127° 0′	26.74	7.49			
	C	[illegible]	[illegible]	127° 6′	25.99	9.61			
	D	70° 37′	82° 56′	126° 0′	25.19	8.19			
Mean values.					25.72	8.15	[illegible]	[illegible]	[illegible]
12 per cent. lead...	F	70° 37′	81° 22′	126° 42′	25.14	10.23	1.00	5.11	86.7
22 per cent. lead...	H	70° 36′	77° 23′	127° 42′	23.30	14.88			
	I	[illegible]	[illegible]	127° 0′	23.06	13.86			
Mean values..					23.19	[illegible]	[illegible]	5.02	81.6
33.5 per cent. lead	J	70° 36′	[illegible]	[illegible]	22.46	16.96	1.69	5.03	79.3
52.5 per cent. lead	K	70° 36′	73° 53′	[illegible]	20.56	18.24	1.86	4.90	76.2
64 per cent. lead..	L	70° 36′	72° 26′	[illegible]	18.98	19.03	1.99	4.79	75.0
76 per cent. lead.	M	70° 36′	69° 58′	[illegible]	16.44	20.36	2.21	4.62	72.0
79.5 per cent. lead	N	[illegible]	[illegible]	[illegible]	[illegible]	20.00	[illegible]	[illegible]	71.2
Pure lead........					[illegible]	[illegible]	[illegible]	[illegible]	69.2

Alloy.		φ.	2ψ.	Δ.	$-(\nu^2-\kappa^2)$.	2νκ.	ν.	κ.	Refl. Power, Per Cent.
				546 μμ.					
Cadmium (pure)....	A	70° 37′	82° 18′	123° 24′	22.32	7.32			
	B	70° 37′	83° 56′	124° 0′	23.52	6.33			
	C	70° 37′	82° 11′	124° 10′	22.81	8.07			
	D	70° 37′	82° 40′	124° 12′	23.20	7.68			
Mean values.......	...	....	....	......	23.16	7.45	0.76	4.87	88.6
12 per cent. lead....	F	70° 37′	81° 24′	123° 36′	22.09	8.64	0.90	4.79	86.4
22 per cent. lead....	H	70° 36′	77° 18′	125° 16′	21.14	13.16			
	I	70° 36′	77° 54′	125° 40′	21.02	12.57			
Mean values.......	...	....	....	....	21.08	12.87	1.14	4.78	83.4
33.5 per cent. lead..	J	70° 36′	75° 48′	126° 36′	21.07	15.38	1.58	4.86	79.0
52.5 per cent. lead..	K	70° 36′	74° 4′	126° 4′	19.25	16.25	1.72	4.71	76.7
64 per cent. lead....	L	70° 36′	72° 13′	125° 17′	16.17	17.11	1.92	4.46	72.2
76 per cent. lead....	M	70° 36′	70° 10′	125° 37′	15.52	18.14	2.04	4.44	71.1
79.5 per cent.......	N	70° 36′	70° 4′	125° 29′	15.38	18.10	2.05	4.42	71.6
Pure lead........	...	....	....	......	14.56	20.68	2.42	4.46	69.5
				404 μμ.					
Cadmium (pure)....	A	70° 37′	82° 12′	109° 6′	12.62	4.00			
	B	70° 37′	85° 23′	107° 18′	12.16	2.22			
	C	70° 37′	82° 11′	109° 27′	12.79	4.07			
Mean values.......	...	....	....	....	12.52	2.76	0.39	3.56	93.1
12 per cent. lead....	E	70° 37′	82° 25′	108° 6′	12.17	3.73			
	F	70° 37′	82° 12′	109° 54′	13.01	4.14			
Mean values.......	...	....	....	....	12.59	3.94	0.55	3.59	85.6
22 per cent. lead....	H	70° 36′	78° 28′	111° 48′	13.11	6.37			
	I	70° 36′	80° 0′	112° 6′	13.63	5.73			
Mean values.......	....	....	....	....	13.37	6.05	0.81	3.74	81.4
33.5 per cent. lead..	J	70° 36′	77° 0′	113° 42′	13.57	7.78	1.02	3.82	78.2
52.5 per cent. lead..	K	70° 36′	75° 5′	113° 15′	12.65	8.58	1.15	3.74	75.2
64 per cent. lead....	L	70° 36′	73° 10′	112° 54′	11.74	9.30	1.27	3.66	72.4
76 per cent. lead....	M	70° 36′	70° 40′	113° 6′	9.56	10.47	1.52	3.45	66.6
79.5 per cent. lead..	N	70° 36′	70° 2′	113° 48′	10.71	10.94	1.52	3.61	68.6
Pure lead..........	...	.....	.....	....	11.17	12.11	1.63	3.72	68.5

Table III.

Tin-lead Alloys.

Alloy.		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Refl. Power, Per Cent.
				579μμ.					
Tin, pure	A	70° 33′	76° 38′	131° 40′	26.24	19.21			
	H	70° 41′	76° 55′	131° 54′	27.24	19.47			
Mean values					26.74	19.34	1.77	5.47	81.1
7 per cent. lead	I	70° 41′	77° 22′	131° 3′	24.68	20.12	1.89	5.32	79.3
21 per cent. lead	B	70° 33′	75° 40′	131° 48′	25.28	20.32	1.89	5.37	79.7
37.5 per cent. lead	C	70° 33′	73° 38′	130° 30′	21.83	20.62	2.03	5.09	76.9
62 per cent. lead	D	70° 33′	71° 18′	129° 37′	18.67	21.28	2.20	4.85	73.9
85.5 per cent. lead	E	70° 36′	70° 47′	129° 30′	17.86	21.46	2.24	4.78	73.1
Pure lead					14.84	22.61	2.56	4.53	69.2
				546μμ.					
Tin, pure	A	70° 33′	76° 4′	131° 27′	25.38	19.53			
	H	70° 41′	77° 13′	130° 7′	25.68	17.32			
Mean values					25.53	18.43	1.73	5.34	80.8
7 per cent. lead	I	70° 41′	76° 22′	129° 11′	24.00	17.27	1.70	5.18	80.3
21 per cent. lead	B	70° 33′	74° 47′	127° 53′	22.15	18.48	1.83	5.05	78.1
37.5 per cent. lead	C	70° 33′	73° 10′	127° 53′	19.54	18.36	1.91	4.81	75.9
62 per cent. lead	D	70° 33′	71° 18′	127° 20′	17.17	18.78	2.04	4.62	73.3
85.5 per cent. lead	E	70° 36′	71° 24′	126° 36′	17.20	18.40	2.00	4.60	73.5
Pure lead					14.56	20.68	2.42	4.46	69.5
				404μμ.					
Tin, pure	A	70° 33′	76° 41′	116° 53′	15.03	9.09			
	H	70° 41′	75° 29′	117° 13′	14.93	10.07			
Mean values					10.98	9.58	1.18	4.05	77.6
7 per cent. lead	I	70° 41′	74° 58′	116° 13′	14.19	9.92	1.25	3.97	76.0
21 per cent. lead	B	70° 33′	76° 32′	117° 42′	15.42	9.52	1.16	4.10	78.3
37.5 per cent. lead	C	70° 33′	74° 44′	116° 42′	13.22	9.51	1.24	3.84	74.9
85.5 per cent. lead	E	70° 36′	72° 7′	115° 30′	12.37	11.11	1.46	3.81	71.5
Pure lead					11.17	12.11	1.63	3.73	68.5

TABLE IV.

Bismuth-mercury Alloys.

Alloy.	$\bar{\phi}$.	$2\bar{\psi}$.	Δ.	$-(\nu^2-\kappa^2)$.	$2\nu\kappa$.	ν.	κ.	Refl. Power, Per Cent.
				579$\mu\mu$.				
Bismuth, pure	. . . .	. . . .	. . . .	9.70	19.72	2.48	3.97	64.4
Bi-Hg (40 per cent. Hg?)	70° 36′	64° 36′	124° 6′	10.32	19.11	2.38	4.00	67.7
Mercury, pure (Meier's results)	. . . .	. . . .	. . . .	16.7	14.2	1.62	4.39	75.3
				546$\mu\mu$.				
Bismuth, pure	. . . .	. . . .	. . . .	9.20	18.04	2.35	3.84	63.8
Bi-Hg (40 per cent. Hg?)	70° 36′	65° 40′	122° 54′	10.92	17.91	2.24	3.99	66.1
Mercury, pure (Meier's results)	. . . .	. . . .	. . . .	15.2	12.3	1.48	4.17	74.9
				404$\mu\mu$.				
Bismuth, pure	. . . .	. . . .	. . . .	7.06	11.80	1.80	3.23	60.6
Bi-Hg (40 per cent. Hg?)	70° 36′	67° 2′	110° 3′	8.33	10.44	1.59	3.29	63.6
Mercury, pure (Meier's results)	. . . .	. . . .	. . . .	9.2	5.8	0.92	3.17	73.3

TABLE V.

Ne^2/m and W.

Bismuth-lead Alloys.

	Per Cent. Lead.	0.	6.	19.	26.4.	48.	61.	75.	86.	100.
Ne^2/m × const	579 $\mu\mu$	131	132	134	133	137	137	137	139	143
	546 $\mu\mu$	133	133	132	146?	124?	137	137	137	142
	404 $\mu\mu$	148	147	149	141	146	144	152	147	149
W × const	579 $\mu\mu$	281	274	276	261	259	252	232	234	223
	546 $\mu\mu$	283	278	279	276	247	247	235	233	223
	404 $\mu\mu$	308	323	309	275	268	265	267	234	220

Cadmium-lead Alloys.

	Per Cent. Lead.	0.	12.	22.	33.5.	52.5.	64.	76.	79.5.	100.
Ne^2/m × const	579 $\mu\mu$	92	94	101	105	112	114	122	120	140
	546 $\mu\mu$	93	93	103	115	114	113	122	121	141
	404 $\mu\mu$	95	99	115	122	123	125	129	137	149
W × const.	579 $\mu\mu$	52	64	97	105	123	152	186	121	223
	546 $\mu\mu$	51	65	100	123	137	156	184	186	223
	404 $\mu\mu$	46	64	92	110	140	162	214	204	229

Tin-lead Alloys.

	Per Cent. Lead.	0.	7.	21.	37.5.	62.	85.5.	100.
$Ne^2/m \times$ const.	579 μμ	125	123	127	125	127	125	143
	546 μμ	134	127	129	125	126	124	141
	404 μμ	136	150	132	150	——	140	150
$W \times$ const.	579 μμ	114	123	126	147	173	179	223
	546 μμ	120	119	138	151	175	171	223
	404 μμ	136	150	132	150	——	182	220

Bismuth-mercury Alloys.

	$\frac{Ne^2}{m} \times$ const.			$W \times$ const.		
	Bismuth.	*Bi — Hg.*	Mercury.	Bismuth.	*Bi — Hg.*	Mercury.
579 μμ......	131	127	92	281	257	135
546 μμ......	133	125	88	283	245	127
404 μμ......	148	129	89	308	242	123

The observational errors inherent in katoptric methods give possible variations of 3 or 4 per cent. in the values of ν and κ, and correspondingly larger variations in $\nu^2 - \kappa^2$ and $2\nu\kappa$. These limits suppose perfect metal surfaces. From an inspection of the values obtained by the writer for different surfaces of the same liquid surface it will be seen that this limit is practically attained. As observations upon different surfaces of solid metals of the same composition differ among themselves by 10 to 30 per cent. in some cases, even for the same observer, the experimental advantages of using liquid surfaces are manifest. There are no scratches or surface impurities due to abrasive material, no differential polishing of the components of an alloy, and no question of variation of surface due to heat treatment. The surfaces are always plane and can be renewed at pleasure.

The determinations made with violet light (404 μμ) were exceedingly difficult to make on account of eye-fatigue. The values of the optical constants for this light are therefore regarded merely as a check on the other determinations.

IX. Discussion of Results.

Interpretation of the above results is most conveniently made on the simple free electron theory of Drude. His conception of the free electrons ricochetting from molecule to molecule under the influence of an outside applied electromagnetic field is inadequate, especially in the light of the more recent developments of the electron theory. Nevertheless, his classic treatment is capable of explaining and coordinating metallic phenomena qualitatively with surprising success.

Drude's[1] equations for the optical constants of the metals are as follows:

$$n^2(1-k^2) = 1 + \Sigma \frac{\theta_h'}{1 - \left(\frac{\tau_h}{\tau}\right)^2} - 4\pi \; \Sigma \frac{m'N}{r^2 + \left(\frac{m'}{\tau}\right)^2}, \tag{1}$$

$$2n^2k = 4\pi\tau\Sigma \frac{Nr}{r^2 + \left(\frac{m'}{\tau}\right)^2}. \tag{2}$$

The first summation in equation (1) is a term wholly due to the molecules of the metal. The other two summations in both equations express the optical effect of the free electrons, being stated wholly in terms of their parameters and τ, the period of vibration of the light used, divided by 2π. In these latter summations, m' is equal to m/e^2, m and e being the mass and charge of each of any group of free electrons. N is the number per cm^3. of each group. r is equal to N/σ, σ being that portion of the total "conductivity" of the metal due to these particular electrons. σ should be equal to the electrical conductivity as usually defined for steady currents.

In this work, the following simplifying assumptions are usually made:

(*a*) In equation (1), the terms $1 + \Sigma\cdot\theta_h'/[1 - (\tau_h/\tau)^2]$ have been assumed to possess a value independent of the free electrons present, *i.e.*, these terms have a numerical value equal approximately to that of $n^2(1-k^2)$ for a heavy insulator. As selective reflection is very small for the metals used in this investigation, n may be taken as about 1.6 and k as 0. Thus $n^2(1-k^2)$ for the molecules of the metal, or its equivalent $1 + \Sigma\cdot\theta_h'/[1 - (\tau_h/\tau)^2]$ will be numerically equal to about 2.5. Since $n^2(1-k^2)$ is a much larger negative quantity for metals, rather wide variations for this assumed value of 2.5 will not seriously affect the final results.

(*b*) The free electrons are assumed to be of one group, *i.e.*, they are negative electrons possessing identical mass, charge, average velocity, etc. The positive electrons are essentially molecules possessing positive charges. Being relatively large and heavy, they contribute practically nothing to the electrical and optical characteristics peculiar to metals. Their optical effect is thus entirely contained in the first summation of equation (1) given in (*a*).

If we divide numerators and denominators of the fractions in (1) and

[1] P. Drude, Theory of Optics (Mann's translation), p. 398

(2) by m'^2 and substitute m/e^2 for m', the above equations become

$$\nu^2 - \kappa^2 = 2.5 - \frac{4\pi \dfrac{Ne^2}{m}}{\dfrac{r^2e^4}{m^2} + \left(\dfrac{1}{\tau}\right)^2}, \tag{3}$$

$$2\nu\kappa = 4\pi\tau \frac{\dfrac{Ne^2}{m}}{\dfrac{r^2e^4}{m^2} + \left(\dfrac{1}{\tau}\right)^2}, \tag{4}$$

where ν and κ have been used for Drude's n and $n\kappa$ respectively. r has been given as equal to N/σ. σ, the electrical conductivity, is expressible in the free electron theory of Drude by $Ne^2/m \cdot T/2$, in which T is the average value of the time between successive impacts of a free electron with successive molecules. This period is equal to the reciprocal of the number of impacts of the electron with molecules per second, and will be the same for all electrons. If we substitute $1/W$ for $T/2$, σ is equal to Ne^2/mW. W is thus a sort of quasi-frequency of impact of the free electrons. r is now given by mW/e^2. If this is substituted for r in equations (3) and (4), and ω for $1/\tau$ (*i.e.*, ω for 2π times the frequency of the light used), these equations become

$$\nu^2 - \kappa^2 = 2.5 - \frac{4\pi \dfrac{Ne^2}{m}}{\omega^2 + W^2}, \tag{5}$$

$$2\nu\kappa = 4\pi \frac{W}{\omega} \frac{\dfrac{Ne^2}{m}}{\omega^2 + W^2}. \tag{6}$$

W and Ne^2/m may be computed from these equations and the values of the optical constants. The reasons for the choice of W rather than T as a free electron parameter will perhaps be evident in the discussion following.

Optical Constants in the Solid and Liquid States.—Figures 3, 4, 5 and 6 show the relations between the optical constants for the solid and liquid states of the pure metals. The data for the solid metals has been obtained from various papers. It is seen that with the exception of cadmium, these constants are roughly doubled by fusion. Figs. 7, 8 and 9 show the variation of the constants $\nu\kappa$ and $\nu^2 - \kappa^2$ for liquids, with the atomic concentration of one component. In general, these are smooth, nonlinear curves. Littleton has assumed that simple mixture in solid alloys will be shown by the straight line variation of these con-

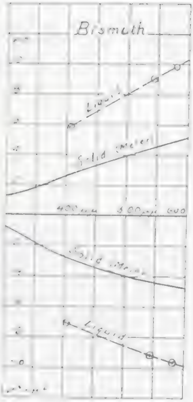

Fig. 3.

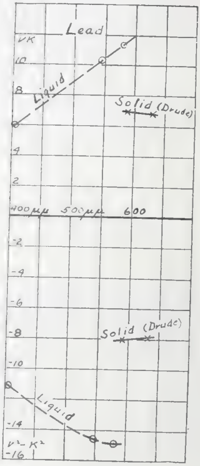

Fig. 4.

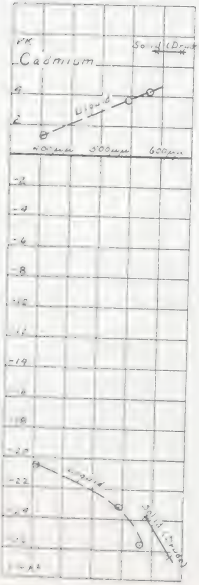

Fig. 5.

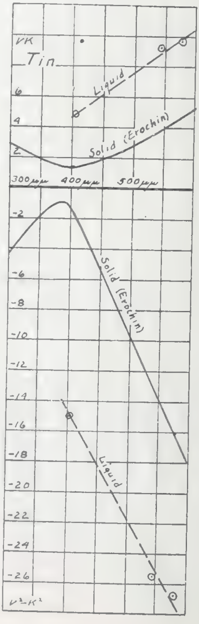

Fig. 6.

stants with the composition. This, of course, will be so where the alloy consists of two types of crystals mechanically mixed.

Theoretical Interpretation of Results.—In Table V. the calculated values of Ne^2/m and W are given for all the pure metals and alloys investigated. The units used are arbitrary. In Figs. 10, 11 and 12 they have been plotted against the atomic concentration of one component, for each series of alloys respectively.

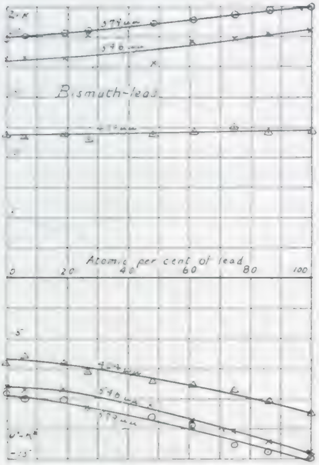

Fig. 7.

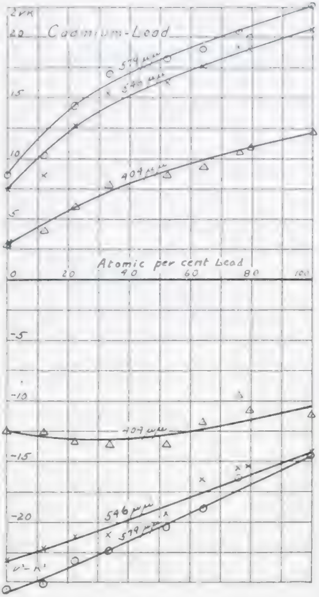

Fig. 8.

Within the limits of error, the values of Ne^2/m calculated from the optical constants for yellow and green light (579 $\mu\mu$ and 546 $\mu\mu$) seem to lie on the same straight line for each series, except for the pure lead points in Figs. 11 and 12. While the results for violet light (404 $\mu\mu$) are altogether too uncertain to be used in determining any functional relationship of Ne^2/m, there seems to be no doubt that in general they lie above the other points. Ne^2/m, however, should be the same, whatever the wave-length of the light used in determining it. The discrepancy is probably due to the following causes: (*a*) the effect of atomic resonance may not be even approximately represented by 2.5; (*b*) selective reflec-

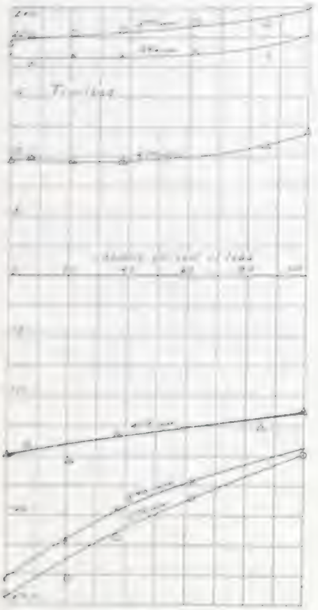

Fig. 9.

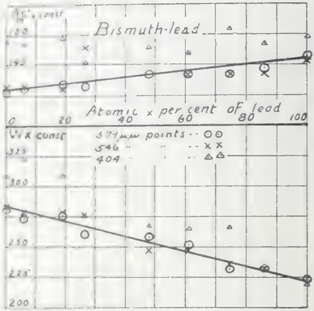

Fig. 10.

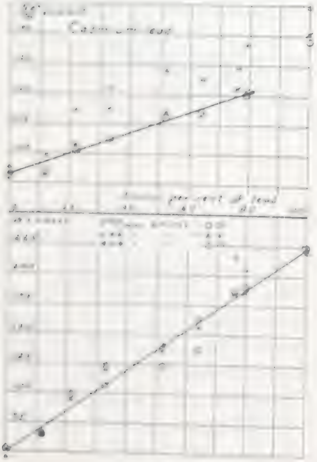

Fig. 11.

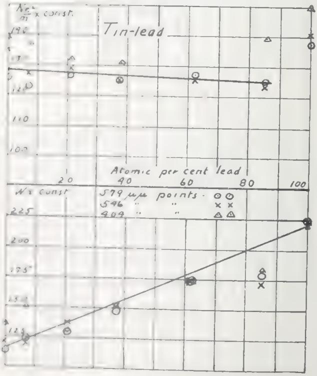

Fig. 12.

tion may be present in the ultra violet, not far beyond the visible. This is the case for most solid insulators. As selective reflection is due to the resonance of bound electrons within the atom, its presence in the atoms of most metals may be inferred. The above effect may be indicated for bismuth by the slight irregularities at the violet end of the solid curves for this metal. In the case of tin, Erochin has placed the center of an absorption band at 340 $\mu\mu$. Selective reflection in the ultra-violet usually increases the value of the term in the expression of $\nu^2 - \kappa^2$ for violet light, which represents the effect of the bound electrons of the atoms, and will introduce a somewhat similar term into the expression of $2\nu\kappa$.

The probable linearity of the variation of Ne^2/m with atomic concentration is to be expected. The molecules of a liquid metal are distinct entities, practically independent of each other. The fields of force of their component electric charges are thus almost entirely internal. The conducting electrons may therefore be regarded as truly "free," and as a definite portion of the metal. Thus each component of the alloy carries to the alloy a certain number of free electrons, identical in characteristics, and the number of these in the mixture is the sum of the numbers present in each component before the alloy is formed.

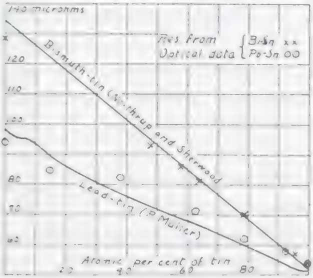

Fig. 13.

The pure lead points in the Cd-Pb and Sn-Pb figures are not collinear with the other points, and the difference can hardly be ascribed to experimental error. The cause of this variation, therefore, probably lies in some peculiarity of constitution of these alloys. Such a peculiarity is indicated by the resistances of this series of alloys, as given by P. Müller.[1] In the tin-lead series, the resistance rises uniformly with the lead content up to about 90 per cent. lead. Beyond this the resistance curve is lifted up in a small but distinct maximum (see Fig. 13). Müller gives the resistances of the cadmium-lead series to 6 per cent. cadmium only, but the same rise is evident. The fall of resistance from the maximum to pure lead is probably due to the anomalous increase in the number of free electrons indicated by the optical results.

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[1] P. Muller, Metallurgie, 7, 755, 1910.

In the solid state, these alloys are solid solutions at the lead side of the phase diagrams. The temperature of 400° at which the observations were made, is not far above the temperature of complete fusion, and it is quite possible that the tendency to atomic grouping shown by the solutions is carried over into the molten state. This tendency is analogous to the formation of an easily dissociated compound, and the process of grouping will result in a similar manner in the absorption of free electrons into the groups. Thus the alloy from 0 per cent. to 90 per cent. lead may be considered as a simple mixture of cadmium (or tin) and this quasi-compound, and the atomic concentration—Ne^2/m curve will be a straight line within this range. The alloy series from 90 per cent. to 100 per cent. lead should act as a mixture of the so-called compound and pure lead, in a similar manner.

Turning to the curves which show the variation of W with the atomic concentration, the agreement of the values of W given by the three lights used is very good, except for alloys rich in bismuth. The differences for this metal series may be due to either or both of the causes given for the Ne^2/m variations. It should be possible to bring the values of both Ne^2/m and W into good agreement for the three lights used, by assuming suitable values of the molecular or bound electron terms in the optical equations. However, in view of the rather large errors inherent in optical measurements on metals, it has seemed hardly worth while to do this.

The linearity of the W curves is striking, and is also a natural consequence of the liquid condition of the alloys. The frequency of impact of a free electron with the comparatively inert molecules ($2W$) is proportional to the "total surface of impact" of the molecules. If we introduce into the assemblage of like molecules of the one metal molecules of another metal which are of a different size, the "total surface of impact," and therefore the frequency of impact of a free electron, are both obviously linear functions of the atomic concentration of either component.

It should be noticed that there is no indication in these curves of any peculiarity of cadmium-lead and tin-lead alloys rich in lead, such as that shown by the variation of Ne^2/m. The tendency towards atomic grouping which would account for this variation cannot be very great. This is shown in P. Müller's work. As the temperature is increased the irregularities of the concentration-resistance curves of these alloys disappear. Owing to this looseness of grouping there is no marked shielding of one atom by another. This will be especially true if the targets of impact are the atomic nuclei. Under these conditions the frequency of impact of any free electron will be unaffected by such tendencies, and the variation of W with atomic concentration will be linear. If true compounds were formed, however, the close association of atoms might be expected to influence this free electron parameter.

Thus the variation of the free electron functions, Ne^2/m and W in these binary alloys and the coherence of results, seem to confirm very strongly the admissibility of the application of the simple form of the electron theory to liquid metals. However, any satisfactory optical theory should be able to show a quantitative relation between the electrical and optical characteristics of metals. Any of these characteristics or any of the parameters of the conducting electrons, should be determinable from a sufficient number of the remainder. For instance, Drude,[1] Schuster,[2] W. Meier[3] and others have calculated the number of free electrons per atom in various solid metals from the optical constants and electrical conductivity. Rubens and Hagen[4] tested the relationship of the electrical conductivity and reflecting power of metals given in the equation $1 - R = 2/\sqrt{\sigma T}$, in which R is the reflecting power, σ the electrical conductivity and T the frequency of the light used. This equation is not valid for visible light but holds very well for the infra-red ($25.5\ \mu$) with one or two exceptions. These exceptions have been held to be due to the neglect of "resonance of the molecules" in the electromagnetic theory of Maxwell, from which the equation is derived. Now Drude's equations, forms of which are used in this paper, are recognized as a better representation of the optical behavior of metals, than Maxwell's original equations. $1 - R = 2/\sqrt{\sigma T}$ may be derived from Drude's equations if we assume W very large in comparison with ω, *i.e.*, that the time between successive impacts of an electron may be neglected in comparison with the period of the light used in the optical determinations. Thus the lack of agreement of Maxwell's equation with facts in the case of bismuth and one or two other metals is probably due to the omission of a term which has nothing to do with "resonance of the molecules."

In general it may be said that when solid metals are used, the data obtained from electrical measurements agree rather poorly with those from optical measurements in the visible spectrum. This may be illustrated very well for the solid state of the metals which were investigated in this work. From equations (5) and (6) we may obtain

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[1] P. Drude, Ann. d. Phys., 14, 677, 1904.

[2] A. Schuster, Phil. Mag., 7, 151, 1904.

[3] W. Meier, Ann. d. Phys., 31, 1017, 1910.

[4] Rubens and Hagen, Ann. d. Phys., 11, 873, 1903.

$$\frac{Ne^2}{m} = -\frac{\omega^2}{4\pi}\frac{(\nu^2 - \kappa^2 - 2.5)^2 - (2\nu\kappa)^2}{(\nu^2 - \kappa^2 - 2.5)}$$

and

$$W = -\frac{\omega 2\nu\kappa}{(\nu^2 - \kappa^2 - 2.5)}.$$

The electrical restivity (in electrostatic units) is Wm/Ne^2 and substituting from the equations above,

$$\text{Res. (e.s.u.)} = \frac{4\pi}{\omega}\frac{2\nu\kappa}{(\nu^2 - \kappa^2 - 2.5)^2 - (2\nu\kappa)^2}.$$

I have used the data of the various writers from which the solid metal curves of Figs. 1, 2, 3 and 4 were drawn to calculate the restivities. These are expressed in microhms and compared with the electrical resistivities of the same solid metals as given by the Smithsonian Tables, as follows:

	Bismuth.	Lead.	Cadmium.	Tin.
Light used	600 $\mu\mu$	600 $\mu\mu$	560 $\mu\mu$	550 $\mu\mu$
Res. (microhms) by opt. methods	238	159	58	76
Res. (microhms) by Smiths. Tables	119	22	7.5	14

The lack of agreement indicated above has been explained on the supposition that the resistivity at frequencies approaching that of light is markedly different from that at ordinary frequencies. Livens[1] and others have developed this functional relation. Owing to the simple conditions existing in molten metals, it should be possible to use their optical constants to gain considerable information as to this possible variation of resistivity, and as to the identity of the electrical and optical parameters given in the elementary equations. On this account I have calculated the resistivities of the pure molten metals from the optical data I have obtained. These and various electron parameters are given in the following table. Only the optical results for yellow and green light were used, those for violet light having altogether too large experimental errors. Meier's[2] results were used for mercury. The resistivities so obtained, are compared with those found by Northrup and Suydam[3] for bismuth, lead, cadmium and tin at 400°. While no particular effort was made to keep the temperature of the liquid metals constant during the optical investigation, it was never very far from this value. The resistivity of mercury at ordinary temperatures was used.

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[1] G. H. Livens, Phil. Mag., 30, 112, 1915.

[2] W. Meier, *loc. cit.*

[3] E. F. Northrup and V. A. Suydam, Journ. Franklin Inst., 175, 153, 1913.

TABLE VI.

	Bismuth.	Lead.	Cadmium.	Tin.	Mercury [illegible]
$Ne^2/m \times 10^{-29}$	132	142.5	92.5	129.5	90
N (No. free electrons per cm.^{3}) $\times 10^{-22}$	14.7	15.9	10.3	14.5	10.0
No. atoms per cm.^{3} $\times 10^{-22}$	2.9	3.1	4.3	3.5	4.1
No. free electrons per atom	5.1	5.1	2.4	4.1	2.5
$W \times 10^{-13}$ [illegible]	282	223	51.2	117	131
Impacts of free electron per sec. $(2W) \times 10^{-14}$	106	84	19.5	44	50
Impacts per period of green light (550 $\mu\mu$)	19.3	15.3	3.5	8.9	9.0
Wm/Ne^2 (resistivity, e.s.u.) $\times 6.60 \times 10^{-7}$	2.14	1.57	0.56	0.90	1.46
Resistivity in microhms from above data	128	94	33.4	54	87.3
Resistivity in microhms from electrical data	134	98	34	52	94
Ratio "optical" to electrical resistivity	.95	.96	.98	1.04	.93

An auxiliary figure (Fig. 13) is also given which compares the resistivities of tin-lead and tin-bismuth alloys, electrically and optically determined. The electrical data for the two series of alloys are taken from papers by P. Müller,[1] and by E. F. Northrup and R. G. Sherwood[2] respectively. The "optical" resistances of the tin-lead alloys were taken directly from the optical results of this series. As the optical characteristics of tin-bismuth alloys were not investigated, the "optical" resistances of this series were calculated from the electron parameters Ne^2/m and W of the pure metal. Both of these are linear functions of the atomic concentration, provided that no compounds are present in the liquid state, and may be easily determined for an alloy of the two metals of any given atomic composition. The quotient of these two will give the resistivity.

From an inspection of the tables and auxiliary figures, it may be seen that, except for mercury, the electrically and optically determined resistivities agree, in every case, within the limits set by unavoidable experimental error. The optical constants of mercury were not determined by the writer and their accuracy is not known, although it is probably good. There is no evidence of any change in the electrical resistivity, even up to the frequencies of light. Certainly any such variation is not greater than 5 per cent. The agreement of the results, both electrical and optical is a strong confirmation of the existence of essentially "free" electrons in these liquid metals. In view of the probable validity of this conception. I have calculated the values of N, the number of free electrons per cm.^{3}, the number per atom, the frequency of impact of the free electrons ($2W$) and the ratio of this frequency to that of green light (550 $\mu\mu$). The number of free electrons per atom necessitated a knowledge of the number of atoms per cm.^{3} For each metal this number is equal to Avogadro's number multiplied by the density and divided by the atomic weight. Avogadro's number was taken as 60×10^{22}. The densities of the molten metals are not accurate, as the temperatures at which they were taken were not given in the tables consulted. To calculate the number of electrons per cm.^{3}, e was taken as equal to 4.77×10^{-10} e.s.u. and m to 9×10^{-28} g. It is evident that the uncertainties of the various constants used in these calculations render the values of the number of free electrons per atom only approximations at best. In addition it is probable that the parameters Ne^2/m and W given here, in reality include constant multipliers. These would be introduced in a more exact development of the free electron theory.

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[1] P. Müller, *loc. cit.*

[2] E. F. Northrup and R. G. Sherwood, Journ. Franklin Inst., 182, 477, 1916.

From certain points of view it would seem that the number of free electrons per atom, or at least per molecule, should be an integer for each metal. The accuracy of the present work is not sufficient to settle this point. On the other hand, the uncertainties of the constants used to obtain these relations, affect all alike, and it is possible to obtain these ratios as integers, within the limits of experimental error, by making small and legitimate changes in the above doubtful constants. The results are certainly not inconsistent with the possibility of these integral relations.

From the agreement of the electrical and optical data in Table VI., it seems that changes of resistivity at light frequencies, and molecular resonance (except in infrequent cases) are negligible factors in determining the phenomena of these liquid metals. I can see no reason why they should be of any greater importance in solid metals, and the discrepancies encountered in the explanation of the optical and electrical phenomena of the solid phase must be due to some different cause. The distinguishing characteristic of the solid metal is the space lattice structure of its crystals. This structure demands that the atoms should have strong external fields of force, binding them into a rigid form. The conducting electrons can hardly wander freely in inter-atomic space, between so-called impacts. From various points of view it is hard to avoid the conclusion that conduction in crystalline solids is due to the "handing along" of these electrons from atom to atom. Thus, in the fundamental equations of motion of a conducting electron in the metallic crystal, a term must be present which is a function of the position of the electron within the space lattice. It is probable that the neglect of such a term is the source of apparently discordant electrical and optical results for solid metals.

The small range of temperature and the limited accuracy of the experimental work made impossible the detection of measurement of any temperature effect on the optical constants. Such measurement would be of value from a theoretical standpoint.

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and many interesting forms of unsymmetrical hysteresis curves can be traced across this area.

This paper is concerned with one such point, viz., *O*, Fig. 1, which represents the condition of the iron when it is completely unmagnetized. The normal magnetization curve starts from this point, rising slowly at first, then more rapidly, and finally more and more slowly.

In explaining this double inflection of the magnetization curve Steinmetz[1] has pointed out that the same thing is also true of the lower branch of the hysteresis curve, and he concludes that "the rising magnetization curve determined by the step-by-step method is thus nothing but the rising branch of an unsymmetrical hysteresis cycle, traversed between such limits that the rising branch of the hysteresis cycle passes through the zero point." And curves are shown[2] where such unsymmetrical hysteresis curves run into, and are continued by, the rising magnetization curve "taken by ballistic galvanometer by the step-by-step method."

Similar curves are shown in text-books[3] in which the unsymmetrical hysteresis curve through the zero point does not agree with the rising magnetization curve as determined by the step-by-step method. In neither case, however, is unmistakable evidence presented that these curves faithfully represent actual observation, rather than a free-hand sketch illustrating the opinion of the writer. It seemed worth while, therefore, to obtain curves from actual measurements which would show the true condition of the iron when brought to the zero point along such an unsymmetrical hysteresis curve. It is shown below that this condition is not that of demagnetized iron, but as there is no resultant magnetic flux it may be described as neutral magnetization.

OUTLINE.

The measurements of magnetic flux were made with the galvanometer-fluxmeter which has been previously used and described.[4] This instrument indicates the full amount of the change in the magnetic flux, even when the last part of this change is slow. The ordinary ballistic galvanometer shows only the change occurring in the first few seconds. Furthermore, the fluxmeter stands at rest after its deflection, and this facilitates an accurate reading. The scale was calibrated by comparison with a standard of mutual inductance, and the ratio of flux to deflection remained constant to within one tenth of one per cent. throughout the period of this investigation.

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[1] Gen. Elec. Rev., Vol. XX., p. 135.

[2] Ibid., p. 138.

[3] *E.g.*, Watson, Physics, p. 716.

[4] PHYS. REV., Vol. 9, p. 415, 1917.

Three grades of iron have been investigated,—cast iron, cast steel, and Swedish iron. Each was in the form of a ring, and was wound uniformly with many turns of wire to carry the magnetizing current. A few turns of wire constituted the secondary circuit, which was connected directly to the galvanometer-fluxmeter. Four different B-H curves through the zero point have been determined for each of these rings, and are shown in the accompanying figures. Instead of long tables of data, the results of the many determinations are shown by the points on the curves.

Demagnetization.

In view of the previous investigation[1] on the demagnetization of iron, each ring was fully demagnetized by many reversals of a slowly decreasing current before each set of measurements was made. With the Swedish iron ring it was necessary to reverse the current as slowly as once in ten seconds, when $H = 3$, or less, and to decrease it to a very small value, to obtain complete demagnetization. Anomalous results were obtained when this precaution was slighted.

It has been suggested that there may be oscillations in the primary circuit when the spark appears upon breaking the current. To avoid this possibility, a special rheostat was constructed by which the current could be reduced to zero by 128 steps, and increased as gradually, at each reversal. Thus the changes were slow enough to allow all eddy currents to die away, and it is certain that the iron was carried around the symmetrical hysteresis cycle corresponding to each cycle of the magnetizing field. The curves obtained after demagnetization by this method are the same as those obtained after demagnetization by simple reversal of the current, *provided*, that sufficient time is allowed between successive reversals.

Normal Magnetization Curves.

The normal magnetization curve, OA, shown by the broken line in the figures, was obtained during the process of demagnetization. After a given value of the magnetizing current had been reversed ten times or more, the change in flux was measured when the current was reversed once again. Half of this change was taken as being the flux corresponding to this value of the current. The points thus determined are shown by the dots along the broken curves in Figs. 2, 3, and 4.

The same curve was also determined by the step-by-step method. Starting with the iron demagnetized, the current was suddenly increased by a definite amount. The corresponding change in the flux was meastized by the fluxmeter, and then a second step was made. These points are shown by the small crosses along the broken line curve, *OA*. They agree so closely with the dots that one line represents both curves.

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[1] Phys. Rev., Vol. 36, p. 384, 1913.

Both the dots and the crosses were plotted on millimeter cross section paper and a fair curve drawn through them. When this curve was retraced for Fig. 1, the broken line, *OA*, was wide enough to cover both sets of points. In order to show in Fig. 1, these points would have to be enlarged so much as to nullify their accuracy, and the result is better shown by the curve. They have been enlarged enough to show in the large scale Figs. 2, 3, and 4.

UNSYMMETRICAL HYSTERESIS CURVES.

The symmetrical hysteresis curve for Swedish iron is shown by *AP*, Fig. 1, for comparison with the unsymmetrical curves. This was ob-

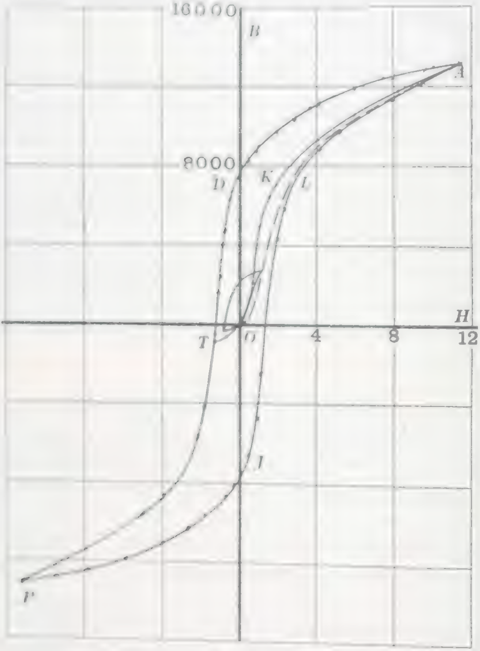

Fig. 1.

Hysteresis curves for Swedish iron, showing the relation of the unsymmetrical hysteresis loops through the zero point, *O*, to the full curve, *AP*. The larger loop is *ADTKA*, as shown in the text.

tained by the direct deflection method[1] in which the location of each point is determined independently of the other points by measuring the difference between it and one of the tips of the curve. The points for this curve are shown by the crosses along *AP*. The dots along the curve show the unsymmetrical loop, *ADTKA*, which was traced in the same manner as the full curve, by measuring the distance of each point from the upper tip, *A*.

In order that the returning branch, *TOK*, shall pass through the zero point, *O*, the lower tip must be chosen at a definite point. If this is too far down the curve *DTP*, the returning branch of the unsymmetrical loop will pass below the zero point. If it is taken too high the returning branch will be above *O*. Whether it passes through *O* or not is determined by whether the change in flux along this curve when the field intensity is changed from zero to its full value is half of the change in flux for a reversal of the same field intensity. After several trials, a value was found for the reversed field intensity that would bring the iron along *DT*, and stop at *T*. From this point the returning branch passes through the zero point.

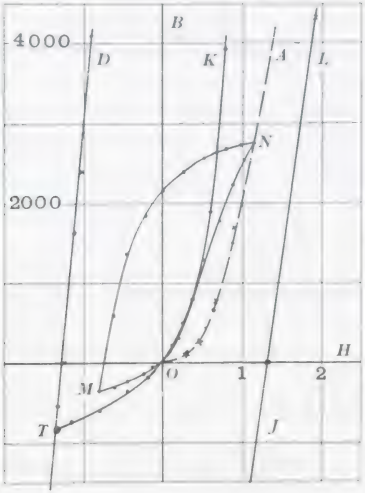

Fig. 2.

Curves for Swedish iron. A portion of Fig. 1, enlarged to show the direction of the unsymmetrical curves near the zero point. Both the smaller loop, *MON*, and the larger loop, *TOK*, are quite distinct from the magnetization curve, *ONA*.

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[1] A. W. Smith, Electrical Measurements, 3d imp., p. 181.

There is not the slightest indication that the returning branch of the unsymmetrical loop runs into the magnetization curve, for it passes through the zero point with a steeper gradient and it continues above the magnetization curve to the end at *A*. This is shown more clearly in Fig. 2, which is the central portion of Fig. 1 drawn to a larger scale.

The smaller unsymmetrical curve, *NM*, was determined by starting from a lower value of the field intensity, as shown at *N*, and carrying it to such a negative value at *M* that the returning branch of the curve would pass through *O*. The ordinate of each point on this loop is determined by measuring the change in flux between the point and *N*, while the abscissa is given by the corresponding value of *H* as computed from the ammeter reading. This curve passes through *O* with a slope slightly smaller than *TO*, but it shows no tendency to run into the magnetization curve.

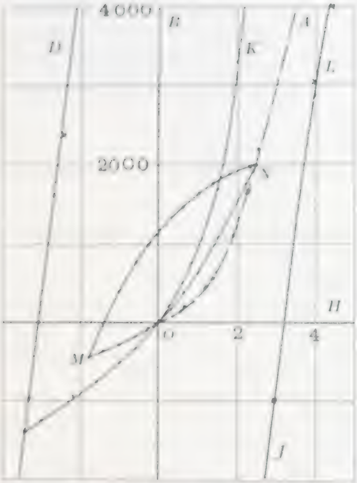

Fig. 3.

Curves for cast steel.

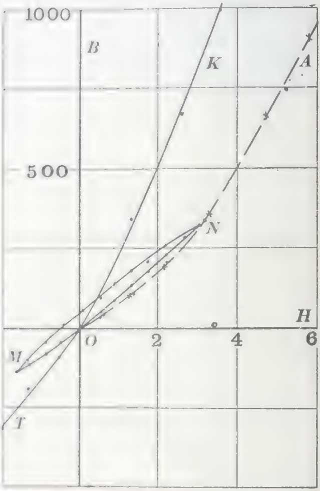

Fig. 4.

Curves for cast iron.

Unsymmetrical hysteresis curves through the zero point. *TOK* is the rising branch of a large loop. *MN* shows a smaller loop. The broken line, *ONA*, shows the normal magnetization curve, which does not coincide with either of the other curves.

Fig. 3 shows a similar set of curves near the zero point for the case of cast steel. These show the same facts somewhat more clearly, as the curves do not run together as closely after leaving the zero point. Not only is the slope at O different for the three curves, but there is little in common throughout their entire lengths.

The curves for cast iron are shown in Fig. 4. On the scale to which these curves are drawn, the full hysteresis loop is wholly outside the limits of the figure. A portion of an unsymmetrical loop, *TK*, passing through the zero point is shown. Also the small loop, *MN*, which even as small as it is, has a slope at *O* that is distinctly different from that of the magnetization curve, *ONA*.

CONCLUSION.

These curves show the manner in which iron, at the point of zero magnetization, responds to an increasing field intensity. When the iron has been brought along one of the unsymmetrical hysteresis loops passing through *O*, the magnetons are thereby somewhat organized, and the curve continues on through the zero point without running into the magnetization curve.

When, however, the iron has been demagnetized by many reversals of a decreasing field intensity, the magnetons are much more disorganized. This results in the low value of the permeability for weak field intensities, and gives the reverse bend at the beginning of the magnetization curve.

As the hysteresis loops, either symmetrical or unsymmetrical, are made smaller the iron is subjected to a smaller negative field intensity, and so is carried a smaller distance below the *OH* axis. The initial portion of the returning branch has the more gradual slope, and when the lower tip is near *O* this means that the whole branch is more flat than it is for the larger loops.

Only when the hysteresis loop has been made exceedingly small does its slope become that of the initial part of the magnetization curve.

University of Michigan,
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FINE STRUCTURE OF THE NEAR INFRA RED ABSORPTION BANDS OF THE HALOGEN ACIDS

BY WALTER F. COLBY

ABSTRACT

Absorption spectra of diatomic gases; quantum theory of the fine structure of the infra-red bands.—The postulate of Bjerrum, that the fine structure of these bands is due to the rotation of the molecules in stationary states corresponding to the quantum relation, has proved very fruitful. The purpose of the present paper is to test the hypothesis by comparing the *theoretical results for the simplest molecular model of the Bohr type* with the experimental results recently obtained by Imes for the *halogen acids.* For HF, HCl, and HBr, the observed interatomic vibration frequencies come out respectively 18, 40, and 47 per cent less than the theoretical, while the computed separations of the pairs of nuclei are respectively 38, 54, and 59 per cent less than the values given by Imes. The variation with mass is explained as a screening effect which has been neglected in the elementary theory. The agreement between theory and experiment is sufficient to lend support to the Bjerrum hypothesis, and suggests the importance of developing a more adequate theory involving fewer simplifying assumptions.

Recent experimental work in the fine structure of absorption spectra in the near infra-red has been greatly stimulated by the very fruitful postulate of Bjerrum[1] concerning the mechanism of this absorption. He explains the structure of the bands in this region as due to the vibration of the atoms in the molecule modified by the rotation of the molecule as a whole about an axis normal to the line of vibration. Following the requirements of the quantum theory, the molecule is assumed to be capable of stationary states of rotation defined by the equation

$$\omega = nh/2\pi I \ .$$

n indicates successive integers. The rotational frequencies are thus

$$\nu_r = nh/4\pi^2 I \ .$$

Calling the interatomic vibration frequency ν_0, the foregoing theory states that absorption will occur at frequencies given by the equation

$$\nu = \nu_0 \pm \nu_r \ .$$

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[1] *Nernst Festschrift*, p. 90, 1912.

Assuming that ν_0 is not modified by the rotational velocity and consequently not a function of n, this equation would require a series of absorption lines symmetrically grouped about ν_0. The series would have two regions of maximum intensity symmetrically placed, corresponding to the most probable value of ω. A small variation of ν_0 with ω would cause a crowding of the bands on one side and a separation on the other. Considerable experimental evidence has been obtained to verify the original hypothesis in these details. It is apparently applicable likewise in the study of band spectra, a success which will greatly strengthen its present position.

The first experimental work which presented these absorption regions with sufficient dispersion to show the fine structure was done by Eva von Bahr in 1913.[1] She used a prism spectrometer and was able to distinguish and measure a considerable number of lines in the bands of a group of diatomic and triatomic gases. The separation of the lines in the simpler spectra gave rotation frequencies which it was possible to identify with absorption lines in the far infra-red, and moments of inertia computed from these and the quantum relation were of the order of magnitude demanded by the kinetic gas theory. With low dispersion these regions appear as doublets. With these and also with the fine structure slightly resolved, von Bahr was able to measure relative intensities and find that the rotation velocities approximated a Maxwellian distribution. When the temperature was raised the doublet separated and its members became flatter and broader. The maximum shifted outward according to the requirements of the Maxwell law for change of most probable velocity with temperature. The recent work, especially that of Sleator[2] and Imes[3] in this laboratory and of Kemble and Brinsmade[4] at Harvard, has extended the dispersion and resolution of the fine structure very materially. Work now in progress confirms qualitatively the earlier statement that the rotational velocities conform quite closely to a Maxwellian distribution, even broken up as they are into the discrete regions of preferred velocities. The great contribution of the new work, however, has been in pushing the resolution to its apparent limit and in determining so precisely the frequencies of these ultimate members. The effect of rise of temperature of the absorbing gas now appears very definitely not to displace these individual lines but simply to sweep the position of maximum intensity outward toward higher values of n. Present work is also using this means of assembling data on the higher members.

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[1] *Verhandlungen der deutschen Physikalischen Gesellschaft*, 15, 710, 1913.

[2] *Astrophysical Journal*, 48, 125, 1918. [3] *Ibid.*, 50, 251, 1919.

[4] *Proceedings of the National Academy of Sciences*, 3, 420, 1917.

The work of Imes has presented the absorption of three of the halogen acids with remarkable precision. It is the object of the present paper to make use of this data in checking the order of magnitude of the variation of ν_0 with n as shown by a molecular model of the Bohr type and to see whether it is possible to express ν_0 for such a model by as strikingly simple a function of n as Imes has found it to be. It will be possible also to check the variation of I with n.

The simplest model of the Bohr type is that first proposed by him,[1] which has the great advantage of being electrically symmetrical. HCl has been chosen as a type, since the results are most complete for that gas. The chlorine atom is assumed to contribute one electron only to the valence ring. The hydrogen atom also contributes one. The H nucleus and the Cl nucleus with remaining electrons are then treated as point charges, an assumption which may depart considerably from the details of the model, but which is sufficiently near for a first treatment. The nuclei thus each possess one positive charge and differ only in mass. Bohr has written the equilibrium conditions for such a system and for this problem it is only necessary to add one term to take care of the molecular rotation. This term is in fact of the same type as the one Bohr has used to indicate the centrifugal force on the electrons in the valence ring. $2x$ indicates the distance between the nuclei, y the radius of the valence ring, M is the reduced mass of the rotating system $[I=M(2x)^2]$, other symbols have their usual significance. The equations are

$$n^2h^2/4\pi^2(2x)^3M+e^2/(2x)^2=2e^2x/(x^2+y^2)^{3/2}$$
$$h^2/4\pi^2y^3m+e^2/(2y)^2=2e^2y/(x^2+y^2)^{3/2}.$$

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[1] *Phil. Mag.*, 26, 857, 1913.

The first term in each equation gives the centrifugal force and recognizes the fact that the angular momentum $=nh/2\pi$. For the electrons, n is set equal to unity. The influence of the molecular rotation on the electrons is neglected. A slight computation shows that the electrons have no appreciable effect on the reduced mass and also that the centrifugal force on the electrons is of a much lower order of magnitude than the electric forces on them parallel to the molecular axis. The equations are easier to discuss if one replaces y by a new variable α by means of the substitution

$$y=x\tan\alpha\,.$$

It is possible then to solve for x and n^2 in terms of α. For $n^2=0$, $\alpha=60°$. α decreases slightly as n^2 grows and becomes $59°27'$ for $n^2=104$. Although it has not been possible to form a closed expression for x in terms of n^2, a curve of corresponding values shows the relation to be very nearly linear for $n^2<100$. One may express these quantities as a series in ascending powers of the very small quantity $(60°-\alpha)$. These series are rapidly convergent and easily obtained. They contribute nothing new to the present discussion but are convenient tools for future work. The following values of the constants were used.

$$\begin{aligned} M&=1.613\times10^{-24}\\ h&=6.55\times10^{-27}\\ e&=4.77\times10^{-10}\\ m&=9.01\times10^{-28}\end{aligned}$$

The linearity between x and n^2 is then given by

$$x=2.017\times10^{-9}+1.23\times10^{-12}n^2\,.$$

Imes gives at $n=0$, $x=6.4\times10^{-9}$. This agreement is not close, but one must note that Imes obtains in the case of HF $x=4.7\times10^{-9}$ and for HBr $x=7.1\times10^{-9}$, and that our equations do not involve M when $n=0$. The observed variation must therefore be due to the screening effect of the inner electrons in the halogen atom. In this calculation the foregoing model should consequently be more nearly checked by HF, which we find to be the case. The centroid of this group of molecules lies always very near the halogen nucleus. We should expect, therefore, that many variations with atomic number must be explained rather by this screening effect than by difference of mass. A model which is otherwise satisfactory but assumes as we have done that the halogen atom may be replaced electrically by a point charge will yield limiting values which the experimental data will approach as the atomic number decreases. As soon as this material is extended and completed the dependence of these frequencies on atomic number can be more satisfactorily studied.

Imes has found an apparent linearity between x^2 and n. It is very difficult to establish a relation here since the variation is so extremely small. He finds that the variation of x from the first to the tenth member is about $50\cdot 10^{-12}$. Our formula gives $123\cdot 10^{-12}$.

To investigate the vibration frequency we shall assume that the amplitudes involved in the absorption in this region are small enough so that we may set the restoring force proportional to the displacement. ν_0 is then given by $\frac{1}{2\pi}\sqrt{F/M}$, where

$$F=d/d(2x)(n^2h^2/32\pi^2Mx^3+e^2/4x^2-2e^2\cos^3\alpha/x^2)\,.$$

A differentiation of the second of the equilibrium equations allows an evaluation of $d\alpha/dx$. Although the calculation is fairly laborious, it is straightforward. One can obtain an expression of ν in terms of α, and with the help of the previous relation between α and n^2 a graphical solution is possible for ν_0 in terms of n^2. Here again the curve is surprisingly closely approximated by a straight line, the equation of which may be written

$$\nu_0=1.4485\cdot 10^{14}-4.63\cdot 10^{12}\,n^2\,.$$

Imes's equation reads

$$\nu_0=0.8661\cdot 10^{14}-0.9\cdot 10^{12}\,n^2\,.$$

We must note again that the observed variation of the constants of this equation with atomic number of the halogen is much too great to be due to difference of mass alone.

For HF $\nu_0=1.1887\cdot 10^{14}-6.20\cdot 10^{12}n^2$.
HCl $\nu_0=0.8661\cdot 10^{14}-0.90\cdot 10^{12}n^2$.
HBr $\nu_0=0.7677\cdot 10^{14}-0.69\cdot 10^{12}n^2$.

The assumed model may again be thought of as an idealization of the halogen acid molecule, which one may expect the actual cases to approach as the atomic number decreases. The discussion of the influence of atomic number will be resumed here also as more measurements are made.

To show that the centers of these line pairs are subject to a variation of the same magnitude as the supposed molecular model would suffer with rotation is striking evidence of the authenticity of the assumption that the fine structure of these bands is due to this rotation. Work is now satisfactorily in progress to extend the number of observed lines of the HCl absorption region at 3.4 μ by raising the temperature of the absorbing gas. It is hoped thus to test these variations with much more material. The second absorption region at slightly less than double this frequency is also being extended and we may hope it to yield more information as to the possibility of a second stationary amplitude of vibration.

A second treatment will endeavor to remove at least some of the foregoing simplifying assumptions. This would consist in using the more satisfactory Kossel model, the at least partial recognition of the space-configuration of the halogen atom, and, most important, the scrutiny of the validity of assuming simple harmonic motion. In respect to this last point, if one assumes an equation of motion involving the square of the displacement the Sommerfeld phase integral still allows a definite statement of the problem of stationary states. By inspecting the standard solution of this new equation of motion one may foresee that the foregoing results will be changed in the right direction. The more complicated solution requires some ingenuity of treatment but may prove valuable in accounting for the higher frequency regions which apparently share the same structure.

PHYSICAL LABORATORY, UNIVERSITY OF MICHIGAN
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JOHN TYNDALL (1820–1893)

By Professor ARTHUR WHITMORE SMITH

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JOHN TYNDALL (1820-1893)[1]

By Professor ARTHUR WHITMORE SMITH

UNIVERSITY OF MICHIGAN

JOHN TYNDALL, British philosopher and physicist, was a most genial and interesting personality. In him a noble and generous nature was combined with a resolute will and lofty principles. He had a fine regard for the rights and feelings of others, and most of his controversies were in defense of truth and justice.

The great ideas of the conservation of energy and the mechanical equivalent of heat were novelties in his time, and his clear thinking and exposition did much to interpret the full significance of these laws. By the publication of his lectures in a style both clear and interesting, and expressed in non-technical language, he reached a large audience, and did more than any other person to secure the wide diffusion of these all-pervading truths that lie at the foundation of physical science.

In the Royal Society's catalogue of scientific papers 145 titles appear under Tyndall's name, and his more extensive writings comprise no less than 16 separate volumes. The complete story of a life so full can not be given in a single evening, and the mere reading of the titles of his many papers would occupy more time than is now allotted to me. But if we can catch a glimpse of his spirit, and gather a bit of inspiration from the enthusiasm with which he worked, this half hour will not be spent in vain.

John Tyndall was born near Carlow, in the southeastern part of Ireland, on the second of August, 1820. Originally of English descent, the Tyndalls crossed to Ireland in the seventeenth century. The elder John Tyndall, although poor, was a man of more than ordinary intellect, and he gave his son a good education in English and mathematics.

To a large extent, Tyndall was a self-made man. His mathematical training enabled him to enter the ordnance survey of Ireland at the age of nineteen, and because of his skill in drawing he was later selected for the English survey. For three years he was a civil engineer at Manchester, and during this time he spent much time in reading and in private study. It was partly through the reading of Carlyle that he was led to abandon the brilliant possibilities then open to a civil engineer, and devote his life to scientific study.

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[1] An address delivered before the Research Club of the University of Michigan at a meeting commemorating the centenaries of John Tyndall and Herbert Spencer, 21 April, 1920.

For some time he was connected with Queenwood College, in Hampshire County, where one of his duties was the instruction of a class in mathematics. His mind was ever on the alert to observe the natural phenomena of daily life, and his teaching was no mere following of text-book routine. It was his custom to give the boys their choice of following Euclid or trying problems of their own devising. The book was never chosen. Their diagrams were scratched on the walls and cut in the beams of the playground, thus showing the lively interest they took in the subject. They found it pleasant to prove by mathematics, and then verify by experiment, that the angular velocity of a reflected beam of light is twice that of the mirror from which it is reflected. And they were startled by the inference that if the earth turned seventeen times its actual speed all things at the equator would lose their weight and have the same tendency to fall upwards as downwards. The days spent with these boys made a deep impression upon Tyndall, and he looked forward to that future day when he might push these subjects a little further and add his own victories to the conquests already won.

The autumn of 1848 found him at Marburg, where, after two years of work, he received the degree of doctor of philosophy. His reputation as an investigator was established by the publication of his work on the magnetic properties of crystals, and the relation of magnetism and diamagnetism to molecular structure. The action of the atoms and molecules held an irresistible attraction for him and every investigation was conducted with molecular arrangement in mind. He was not satisfied with a few typical examples, but he examined nearly a hundred natural crystals and the entire collection of artificial crystals in the laboratory of Professor Bunsen. The subject was studied from every side until he had obtained a clear conception of all the conditions involved, and was able to formulate the general law.

Faraday had just published his researches on the behavior of crystals in taking a definite position when suspended between the poles of a strong magnet. "This force," he says, "appears to me to be very strange and striking in its character . . . for there is neither attraction nor repulsion."

It required long and patient effort to bring under the dominion of elementary principles the vast mass of facts which experiments had brought to light, but the more he worked at the subject the more clearly did it appear to Tyndall that the action of crystals in the magnetic field was due, not to some new and unknown force, but to the modification of the known forces of magnetism and diamagnetism by the crystalline structure. It *was* true that the forces were neither attraction nor repulsion, taken singly, but it was *both*, thus producing a torque which turned the crystal into a determined position. The painstaking observations and the simply stated conclusion showed the qualities for which his work was ever distinguished.

Shortly after his return from Marburg he was appointed professor of physics in the Royal Institution, where Faraday was then director. Seldom have two men worked together so harmoniously as did Tyndall and Faraday during the years that followed. Their relationship from first to last was like that of father and son, and when Faraday died, fourteen years later, Tyndall succeeded him as director of the Royal Institution.

It was at this time also that he became acquainted with Spencer, who was about his own age, and with Huxley who was five years younger. This was the beginning of the most intimate of friendships. On all sorts of minor topics they were liable to differ in opinion, and they never hesitated to criticize each other; but the fundamental harmony between them was profound, for each cared immeasurably more for truth than for anything else. It was no small factor in his life for Tyndall to enjoy the friendship of these two men.

Not all of the investigations of Tyndall were carried out in the laboratory, for he was always awake to the events of daily experience. Even the "spirits" did not escape his observation, and it is especially interesting at this time to read of Tyndall's experience in this field.

The spirits themselves named the time and place of meeting, which proved to be a dinner at a private residence near London. The medium—a delicate looking young lady—was seated next to Tyndall. He records a bit of the conversation. He asked the young lady if she could see the curious things he had heard about—the light emitted by crystals, for example. "Oh, yes," she replied, "but, I see light around all bodies."

T. "Even in perfect darkness?"

Med. "Yes; I see luminous atmospheres round all people. The atmosphere which surrounds Mr. C. would fill this room with light."

T. "You are aware of the effects ascribed to magnets?"

Med. "Yes; but a magnet makes me terribly ill."

T. "Am I to understand that, if this room were perfectly dark, you could tell whether it contained a magnet, without being informed of the fact?"

Med. "I should know of its presence on entering the room."

T. "How?"

Med. "I should be rendered instantly ill."

T. "How do you feel to-day?"

Med. "Particularly well; I have not been so well for months."

All the while there was in Tyndall's pocket, within six inches of her, a magnet; but he felt that nothing would be gained by showing it.

On the whole the evening was a dull one, but towards the end the spirits were asked to spell the name by which Tyndall was known in the spirit world. As the alphabet was slowly repeated a knock was heard when the letter P was reached. Beginning again, the letter O was knocked down. The next letter was E.

The knocks seemed to come from under the table, and Tyndall asked permission to go underneath to assure himself of the origin of the sounds. He remained under that table for a quarter of an hour, and was sure that no sound could be produced without his being able to locate its source. The spirits were urged and entreated to finish the word, but they had become dumb, and could spell no more. Tyndall then returned to his chair, but not without a feeling of despair regarding the prospects of humanity, never before experienced.

The spirits, however, resumed their spelling, and dubbed him, "Poet of Science." More than once after this he accepted invitations to be with the spirits. His comment is, "they do not improve on acquaintance. Surely no baser delusion ever obtained dominance over the weak mind of man."

In the autumn of 1854 Tyndall attended a meeting of the British Association at Liverpool, and at its close he took the opportunity to visit North Wales, where he saw the slate quarries. It interested him to see how readily the rock split open in parallel planes, like wood before an axe. The explanation that these were the layers in which the material was deposited did not satisfy him. Consultation with geologists showed him that the planes of cleavage were not those of stratification, and further investigation on numerous substances convinced him that the cleavage was caused by the effects of pressure.

Two years later these phenomena were made the subject of a lecture at the Royal Institution. His friend Huxley was present, and suggested that this aspect of slaty cleavage might have some bearing on the laminated structure of glacier ice. They were both going to Switzerland that summer, and they arranged a joint excursion over some of the famous glaciers, where they could observe together the veined structure of the ice.

No man knows, when he commences the examination of a physical problem, where it will lead him. For Tyndall this was the beginning of many visits to the Alps, where he continued the study of glaciers for many summers. He satisfied himself that the veined structure was due to pressure, but he was especially interested in learning how a crystalline solid like ice could flow like a liquid. He pointed out the inadequacy of earlier theories, and showed by experimental demonstration that the flow was due to continued minute fracture and subsequent refreezing of the ice.

But once in Switzerland, the fascination of the mountains claimed him, and he became an Alpine enthusiast. Summer after summer he returned to conquer some untrodden Alp, or continue an unfinished investigation. The ascent of Mont Blanc was not complete without planting thermometers at several stations to record the cold of winter while he was absent. Nor was science alone to benefit from these excursions. The volumes that record his experiences are gems of literature, pervaded from cover to cover with the vigor and freshness of the Alpine air.

Tyndall always considered original investigation to be the great object of his life, and his most extensive researches are those in the domain of radiant heat. These experiments were stimulated by the conviction that not only the physical, but also the molecular, condition of bodies probably played a very important part in the phenomena of the radiation and absorption of heat. He wanted to show the physical significance of an atomic theory which had been founded on purely chemical considerations, and this object was continually kept in mind. Radiant heat was used as an instrument to explore molecular condition, and to bring clearly into view the astonishing change in physical properties when the atoms of simple gases unite to form more complex combinations.

As new advance often awaits the production of new instruments, so Tyndall's first requirement was a galvanometer of increased sensitiveness. Having made this galvanometer, and also a sensitive thermo-pile, he proceeded to examine the absorption of radiant heat by various gases. The gas to be examined was placed in a long tube, closed at each end with windows of rock salt. The source of heat was a copper cube filled with hot water. The heat radiating from this copper box passed through the gas in the tube and fell upon the thermopile placed just outside the farther window. The other face of the thermo-pile was warmed from a second source, similar to the first. When the tube was empty, the galvanometer pointed to zero. When the tube was filled with gas, if the molecules possessed any power of intercepting the heat waves, that side of the thermo-pile would receive less heat, and the galvanometer would show a deflection corresponding to the amount of heat thus absorbed by the gas.

Examined in this manner, dry air, oxygen, nitrogen, and hydrogen showed a very slight absorption of the radiant heat. But when in chemical combination, the astonishing fact appeared that carbon dioxide absorbed nearly 1,000 times as much as dry air. Nitric oxide absorbed 1,600 times as much as either nitrogen or oxygen. And ammonia absorbed 5,500 times as much as either of its constituents. To make sure that these results were real, and that errors in the method of observation, or impurities in the gases used, did not mask the true effects, required some thousands of experiments. Observations were repeated again and again, and under various conditions, until he was thoroughly familiar with all the factors that could affect the result. And conclusions were not published until the experiments had convinced him that they were correct.

The case of aqueous vapor in the air proved so interesting and important that a special series of experiments was made upon it. Not only was the air of London examined, but to avoid possible errors due to the effect of local impurities, air was brought from the country and from the seashore. This air, containing the normal amount of aqueous vapor, absorbed 70 times as much heat as air from which the moisture had been removed.

The importance of these results are manifest when they are stated in a different way. It appears from this that the aqueous vapor which exists within ten feet of the earth's surface on a day of moderate humidity is sufficient to absorb 10 per cent. of the entire terrestrial radiation, a considerable portion of which is thus returned to the earth. He thus explained the burning heat by day, followed by the enormous chilling at night, in those places that are not protected by a blanket of moist air. In a general way, this has been referred to the purity of the air, but this purity consists in the absence of the transparent vapor, rather than that of smoke or other visible constituent.

Thus a comparatively slight change in the variable constituents of the atmosphere, by permitting free access of solar heat to the earth and checking the outflow of terrestrial heat into space, might produce changes of climate as great as those which the discoveries of geology reveal.

An extension of this inquiry led him to investigate the absorption of heat by various liquids and their vapors. The behavior of these vapors placed them in a definite order of relative absorption. For heat of the same quality, and using equivalent amounts of the different liquids, he proved that the liquids occupied the same order as their vapors. This led him to the conclusion that the act of absorption is molecular, and that the molecule maintains its power as an absorber and radiator in spite of its change from liquid to vapor. Later he considered this action as due, in large part, to the atoms composing the molecule, rather than its being solely a property of the molecule as a whole.

In another series of experiments the source of radiant heat was a flame of burning gas. The radiation from the hydrogen flame possessed a peculiar interest, for he thought it likely that the resonance between its periods of vibration and those of the cool aqueous vapor of the air might be such as to cause the atmospheric vapor to exert a special absorbent power.

His surmise in this respect was justified, for he found that 20 per cent. of the total radiation from the hydrogen flame was absorbed by 50 inches of *undried* air, whereas only about 6 per cent. of the radiation from a hot platinum spiral was thus absorbed. Nor was this resonance confined to aqueous vapor. The dried air, which was now transparent to the hydrogen flame, was able to absorb 14 per cent. of the heat from a flame of carbon monoxide. Air from the lungs, with the moisture removed, was able to intercept 50 per cent. of the entire radiation from the carbon monoxide flame.

As a result of these investigations, carried out with extreme care and in great detail, he showed the very intimate relation between the absorption of heat and the molecular condition of the absorbing body.

In connection with these experiments, he also showed that those bodies that were the most efficient absorbers of radiant heat were likewise the best radiators of that same heat.

But while we are greatly indebted to Tyndall for the new knowledge which he discovered in the domains of heat and other branches of physics, his name will continue to be loved and remembered even more for the interesting lectures in which his methods of research were explained to public audiences, and the fundamental principles of science made clear to them.

It must have been a delight to listen to him. He was famed for the charm and animation of his language, for lucidity of exposition, and singular skill in devising and conducting experimental illustrations. Both he and his younger friend Huxley were popular with the London audiences, but they were very different. Huxley convinced his audience and compelled their assent; Tyndall carried them with him. They could not help agreeing with Huxley even if they did not wish to do so; they wished to agree with Tyndall if they could. It was the aim of Tyndall to rise to the level of his subject from a basis so elementary that every one in his audience could comprehend it, and then to lead them on by experimental demonstrations to a more complete understanding of the truths of Nature.

In the autumn of 1872 he came to America, where, in several of the eastern cities, he delivered a series of lectures on "Light." His success as a lecturer was complete. At first he was somewhat in doubt regarding the intellectual level that might be expected of the audiences, but he received early warning to talk the same as he would at the Royal Institution. One who heard him says: "It was a rare treat to hear him lecture. His illustrative experiments were beautifully done, his speech was easy and eloquent, and his manner, so frank and earnest and kindly, was extremely winning." His reception throughout was that of a friend by friends; and he looked back upon his visit as a memory without a single stain of unpleasantness.

The noble nature of the man and his unselfish devotion to the science he loved is shown by his attitude towards financial reward. This lecture season brought him about $13,000 over his actual expenses, but he would not take a cent of it. He left it all in the hands of trustees as a fund for the benefit of science in America. At the present time this fund is in the form of three graduate fellowships in physics—at Harvard, Columbia, and the University of Pennsylvania. It is of interest to recall that one of our own men has recently enjoyed one of these fellowships.

Tyndall, like most of his friends, was a reverent agnostic. He did not believe that the ultimate truths of the universe could be expressed in words, or that our limited and finite intelligence could as yet comprehend them. His writings, however, contain many phrases which show that he was familiar with the books of Holy Scripture. And often, after a Sunday evening tea, he would join his friends in the singing of psalm tunes.

On the question of miracles, he did not deny their possibility, but he compares, for example, the horse power involved in stopping the sun and moon (or was it merely the rotation of the earth?) with the feeble efforts expended by Joshua and his men in pursuing the five kings of the Amorites. And with characteristic consideration for the author, he points out that for him the sun was only a moving lantern, whose motion could be varied at the will of the appropriate authority.

His views on the great question of the relation between science and religion were expressed in his presidential address before the British Association at Belfast. In this address he outlined the fortunes of science from the times of the Greeks and the Moors, and depicted the struggle of truth against ignorance and superstition. Tracing back the theory of Darwin to the beginnings of life, he saw only the unbroken workings of Nature, extending beyond the range of experimental evidence, and this led him to the conclusion that the possibility of life must have existed in the atoms of the nebulæ.

He strongly maintained the claims of science to discuss such questions fully and freely in all their bearings, whatever the results might be. Such an address, delivered at the present time, would cause scarcely a ripple of dissent, but at that time it brought down on his head the severe criticism of those who differed from him, and a three days fast was proclaimed to keep infidelity out of Ireland.

An accident in the Alps may have been the cause that turned his mind to investigations in another direction. Having taken a shower bath under the cascade of an Alpine stream, he was returning for his clothes when he slipped and the sharp granite pierced his shin. Dipping his handkerchief in the clear water of the stream he bound up the wound and limped to his hut, where he lay quietly for several days. There was no pain, and upon removing the bandage the wound was found to be clean and uninflamed. But it soon became inflamed, and he had to be carried on men's shoulders to Geneva, where for six weeks he was confined to his bed.

About this time there was considerable dissension regarding the spontaneous generation of life, and Tyndall could not let such a question of fact pass by without adding his own clear logic to the discussion.

In the investigations on radiant heat it had been necessary to use air from which all traces of floating dust had been removed. A sensitive test of such purity was found in a concentrated beam of intense light, which rendered visible particles smaller than any microscope could detect.

Convinced that the reported cases of spontaneous generation of life were due to infection from the air, he wanted to try the effect of this optically pure air. Fifty wooden chambers were built, with windows on each side for the passage of a strong beam of light. When this showed that the air within was free from floating particles, various infusions of meat and vegetable were introduced in open test tubes and properly sterilized. There was no shade of uncertainty in any of the results. All of the infusions remained pure and sweet, although some of them remained freely exposed to the air in the chamber for over a year. Out of a total of 500 chances, there was no appearance of spontaneous generation. But when the air from the laboratory was allowed to enter the chambers, the infusions swarmed with life in two or three days.

Believing in the germ theory, and realizing that in certain stages of development the germs are more readily destroyed by heat, he devised the method of sterilization by repeated heating. In this method the infusion is brought to the boiling point, and then set aside for ten or twelve hours, after which it is brought to the boiling point again. Successive heatings in this manner destroyed the most resistant germs, three minutes of repeated boiling being more effective than 300 minutes of continuous heating.

In recognition of these researches he was given the degree of M.D. by the medical faculty of Tübingen.

At the age of 55 he married the charming and accomplished daughter of Lord Hamilton, whom he met during one of his Alpine excursions. They were companions in all things, living in his rooms at the Royal Institution, and spending their summers among his old haunts in the Alps. But his later years were marred by ill health and sleeplessness, and by accident, one evening in 1893 he took an overdose of chloral, from the effects of which he never awoke.

No other man had done more by research, lectures and writings, to discover and disseminate a sound knowledge of natural phenomena. And because there was no sacrifice of truth for popularity, the books he wrote half a century ago are classics at the present time.

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ON THE ABSORPTION SPECTRUM OF HYDROGEN CHLORIDE

BY WALTER F. COLBY AND CHARLES F. MEYER

ABSTRACT

Hydrogen-chloride absorption band, 3.16 to 3.70 μ.—Because of the great theoretical interest attached to the absorption spectrum of HCl, the authors have undertaken to add experimental data. For most of the observations an absorption chamber 60 cm long which could be heated to incipient redness was used, since Paton had found that as the temperature is raised the number of observable lines is increased while there is no *shift due to temperature*. These results were confirmed. The mean *wave-numbers for 28 lines*, 20 of which have shorter wave-lengths than the center of the group, are given in Table I. The *law of spacing* is not parabolic, as has been supposed, but a cubic term is found to be necessary. The wave-numbers are given by the equation $\nu=28{,}863.60+205.82\ n-3.082\ n^2-0.0165\ n^3$, the mean difference between observed and calculated being 2. The cubic term cannot be due to overlapping of lines at the base. The results obtained by Paton at 250° C. have been reduced. An explanation of the deviations from Imes's results is suggested. Only slight evidence of the *existence of a satellite* on the long-wave-length side of each line was obtained. No compensation chamber was used in these experiments, as a direct test showed it to be superfluous.

The absorption of hydrogen chloride falls into two regions, one extending from 3.35 μ to 3.85 μ (see Fig. 1*b*), and the other from 1.73 μ to 1.83 μ (Fig. 1*a*). The second region falls at approximately twice the frequency of the first and is less intense, whence it has come to be known as the "harmonic," and the first as the "fundamental." In each region the absorption consists of numerous lines, regularly but not uniformly spaced. The only precise measurements which have been made upon these lines were made by Imes,[1] who worked with the absorbing gas at room temperature, as did previous investigators.[2]

Some work on the "fundamental" carried out by Mr. Paton,[3] with the absorbing gas at a temperature of 250° C., showed that as the temperature of the gas was raised, the individual lines retained their position as nearly as could be measured, but that through a redistribution of intensities of absorption the number of observable lines was increased. This was to be expected on the basis of the rotational theory now commonly held for this type of absorption.

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[1] *Astrophysical Journal*, 50, 251, 1919.

[2] Brinsmade and Kemble, *Proceedings of the National Academy of Sciences*, 3, 420, 1917, and Eva v. Bahr, *Verhandlungen der deutschen physikalischen Gesellschaft*, 15, 1150, 1913.

[3] *Physical Review*, 15, 541, 1920.

The absorption spectrum of hydrogen chloride is of great theoretical interest, and for this reason the authors have undertaken to add to experimental data existing upon it. The present paper deals with what has thus far been done upon the "fundamental." Certain points which are of interest have been established, but other points remain unestablished, and no work has yet been done upon the "harmonic." It is hoped to do something more in the future with hydrogen chloride and with the other hydrogen halides.

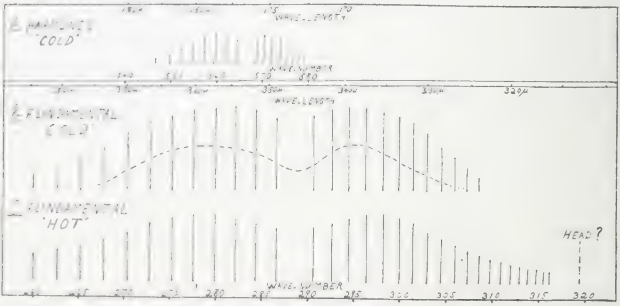

FIG. 1

The apparatus is similar to that used by Imes, and we have used the same 7500-line grating. The absorption chamber consists of a tube of high-temperature glass kindly furnished by the Libby Glass Company. It is 60 cm long and 8 cm in internal diameter and is provided with mica windows. Provision is made for heating electrically, and when working with the gas "hot," the tube was heated to a glow which could be just seen in a darkened room.

Some measurements have also been made with the gas "cold" (room temperature), some with the 60 cm chamber, some with

Imes's chamber 16 cm long, and some using a still shorter chamber 4 cm long.

The wave-lengths of twenty lines on the side of the center toward short wave-lengths, and eight lines on the opposite side of the center have been measured. The center is marked by the absence of one line in the otherwise regular spacing. The lines on the side of short wave-lengths were measured first, and when plotting between n, the number of the line counted from the center, and ν, the wave-number, it was possible to fit these lines so closely to a parabola that it was believed that the spacing of the entire band would be represented by a parabola. This belief was expressed in a paper given before the Physical Society at Cleveland last November. But when the eight lines on the other side were measured, it was found that these rapidly deviated from this parabola, and a little consideration made it clear that it would not be possible to fit a parabola to the entire band. The results of the measurements are given in Table I. The first column on the left gives the number of the line, which, on the side of short wave-lengths, is taken as positive and on the side of long wave-lengths is taken as negative; these will in future be referred to respectively as the positive and negative sides. The measured wave-numbers are given in the second column. The wave-numbers given throughout are "waves per decimeter." This unit is chosen

TABLE I

n	ν Measured	ν Computed	Difference	n	ν Measured	ν Computed	Difference
−8........	27031.	27028.	3.	7........	30148.	30146.	2.
−7........	278	277.	1.	8........	309.	305.	4.
−6........	520.	521.	−1.	9........	453.	454.	−1.
−5........	760.	760.	0.	10........	597.	597.	0.
−4........	991.	992.	−1.	11........	732.	733.	−1.
−3........	28217.	28219.	−2.	12........	858.	861.	−3.
−2........	437.	440.	−3.	13........	984.	982.	2.
−1........	652.	655.	−3.	14........	31095.	31096.	−1.
1........	29065.	29066.	−1.	15........	198.	202.	−4.
2........	265.	263.	2.	16........	298.	300.	−2.
3........	459.	456.	3.	17........	388.	391.	−3.
4........	636.	637.	−1.	18........	481.	474.	7.
5........	816.	814.	2.	19........	554.	549.	5.
6........	986.	984.	2.	20........	615.	616.	−1.

as it is convenient in this discussion, and a change of one wave per decimeter in this region means very nearly a change of one A in wave-length.

In passing out from the center on the positive side, the lines crowd more and more closely together, as can be seen in Figure 1. It was hoped that by raising the temperature of the gas sufficiently, and thus raising the absorption in the lines of higher number, it might be possible to detect a definite head to this absorption region. The existence of a head has not been established, but we hope to use still higher temperatures in the future with a view to searching for it again. The possibility of developing a head on the positive side has caused us to devote most of our attention to measurements of lines on this side. Moreover, on the negative side, after about the twelfth member, the lines fall into a region of absorption by water-vapor, and this complicates the making of measurements.

The eight lines which have been measured on the negative side, and the first eighteen of the twenty on the positive side, have been fitted to a cubic. The equation of the cubic is:

$$\nu = 28863.60 + 205.8239n - 3.081809n^2 - 0.01648171n^3.$$

The nineteenth and twentieth lines were not included in the computation, but they fall satisfactorily on the extrapolated curve. The values calculated according to this cubic are given in the third column of the table, and the differences between measured and calculated values are given in the fourth column.

In Figure 2, curve II, are plotted the residuals obtained after subtracting the arbitrary parabola

$$\nu^1 = 28880.24 + 204.271n - 3.33654n^2$$

from the cubic. The plotted points show the residuals obtained after subtracting the same parabola from the measured wave-numbers. Now if the spacing of the lines were truly parabolic, then we should still have a parabola left after subtracting a parabola, and it is evident that this is not so.

The wave-numbers given in Table I are in general not the result of a single measurement of the position of a line. On some lines as many as six measurements were made. There were sixty-seven measurements made in all with the gas "hot," and twenty-seven made with the gas "cold." No systematic shift due to temperature has been observed and, in making up the averages of column 2 of the table, fourteen measurements with the gas "cold" were included. Something more will be said below regarding "cold" measurements.

The above-mentioned parabola has also been subtracted out of Imes's measured wave-numbers and the residuals have been plotted. Figure 2, I, is a smooth curve going through these points; the points themselves have been omitted to avoid confusion of the diagram. It will be noted that the differences between Imes's values and our own are rather large on the positive side, and this we measured first. We spent much time in trying to reconcile the two sets of data, and at first believed that some systematic error had crept into one set of determinations or the other. A somewhat faulty determination of the spectrometer constant may account for a portion of the differences. The spectrometer constant is determinable to about 0.007 per cent, so that two faulty determinations in opposite directions might account for four units. Again, a faulty determination of the position of the central image of the grating is to be considered. Our practice in determining the position of the central image has been to pass the central image over the thermopile slit, making settings every half-minute of arc,

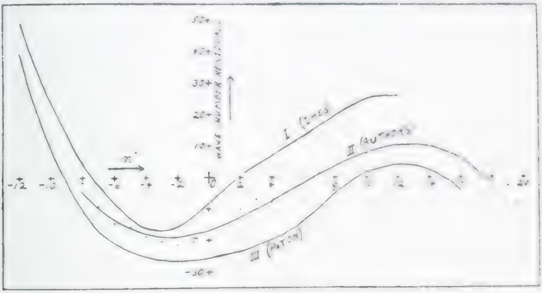

FIG. 2

and taking galvanometer readings at each setting. The intensity of the beam of infra-red radiation is cut down in this case by placing a piece of tissue paper across the beam just before it enters the first slit of the spectroscope; otherwise the galvanometer would go off the scale. The positions of the central image determined in this way have been checked by making five measurements upon absorption lines with the grating turned first to one side of the normal and then to the other. In every determination the check was quite satisfactory. On the other hand, Imes determined the position of the central image visually and did not make any very careful check upon the visual method as applied to his thermopile, and as it frequently happens that the true position of the central image differs slightly from the one visually determined, it may be that some error has crept into his results from this source. But the entire differences between his values and ours cannot be satisfactorily explained as experimental error.

There is probably a real shift in Imes's determinations as compared to ours. There are several causes which may be operative in producing shifts. In the first place, there is the slope of the continuous background which is very marked in Imes's curves. In Figure 1*b*, the waved broken line represents this continuous absorption. It is absorption between the lines due to overlapping at the base. If we consider the sixth line, then the fifth and seventh overlap with it at the base, and as the fifth is a more intense line than the seventh it will overlap more, and there will be a shift toward the fifth line. The magnitude of this shift for a given line will depend upon the numbers of molecules causing absorption in the adjacent lines, and these numbers depend upon the mass of gas in the path, and upon the temperature which affects the distribution of rotational velocities. The mass of gas in the 60 cm chamber "hot" would be about four-thirds that in the Imes chamber, since the chamber is four times as long and the absolute temperature is about three times that of the gas "cold." But the temperature distributes the rotational velocities more evenly, so that the slope of the continuous background is less steep in the 60 cm chamber.

Secondly, it may well be that the absorption lines thus far observed in the "fundamental" do not represent the ultimate structure of the absorption. In the "harmonic" a faint satellite was observed by Imes on the side of long wave-lengths of the more prominent members, Figure 1*a*. The satellite has been explained by Loomis[1] as being due to an isotope of chlorine, and if this explanation is correct it should also be present in the "fundamental." But our definition may be just insufficient to detect it, and the measurements may give the position of a composite of the strong line and this satellite. The position of maximum absorption for this composite would, on account of the exponential law of absorption, shift somewhat with varying numbers of molecules taking part in the absorption, though the ratio of the number of molecules affecting the strong line and the satellite may be supposed constant under all conditions.

Shifts due to overlapping and due to the satellite would affect the law of spacing. But consideration makes it clear that the elimination of the effect of overlapping cannot change the law into a parabola, and we have experimental evidence that it does not. It is somewhat premature to speculate upon the effect of elimination of shift due to the hypothetical satellites, as they may be spaced differently than Loomis supposes.

The accepted formula for absorption bands in this region is of a parabolic type

$$\nu = c_0 \pm c_1 n + c_2 n^2$$

either by the Bjerrum postulate or by the more recent and more satisfactory theory of Sommerfeld-Lenz. In both theories c_0 is dependent on the atomic vibration-frequency and is by far the largest contribution of the three terms. Loomis has pointed out that in the case of HCl the heavier isotope of Cl will produce a satellite with a ratio of frequency 1330/1331 to the predominant line. This ratio is the square root of the ratio of the reduced masses and affects c_0. As an extension of this idea one would likewise expect a variation of c_1: there would be not simply a series of equally spaced doublets, but the separation would grow with order on the positive side and decrease with order on the negative side. The effect on c_1 is due to a difference in the moments of inertia. The contributions of this term would therefore have a ratio of 1330 1332, the ratio of the reduced masses. The term itself, however, is of a lower order than the first and we could only hope to detect its contribution in the case of the higher values of n. The separation due to c_0 is 21.7, and that due to c_1 is 6.3 for $n=+20$. Together they produce a separation of 28.

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[1] *Astrophysical Journal*, 52, 248, 1920.

A word should be said regarding the possibility of shift due to temperature. None is to be expected theoretically, and none has been observed, but individual measurements of a line frequently differ by eight or ten units and sometimes by larger amounts. It would be necessary to measure a given line or lines a number of times "cold" and a number of times "hot," and under conditions especially chosen to avoid all possibility of shift from the two causes mentioned above, before one could conclude that there is no shift as great as three or four units due to temperature. The measurements with the 60 cm chamber "cold" probably fulfilled these conditions approximately. They were made in the very beginning of our work as preliminary measurements. We at that time drew off gas from the chamber by means of an aspirator to prevent it from escaping into the room, and drew air from the room into the chamber so that it was by no means filled with gas.

Four lines on the negative side have been measured "cold" with Imes's chamber. The wave-numbers agree closely with Imes's values. We have not undertaken to map the entire region in this way as the labor involved would be considerable and would show nothing of great value. The measurements which were made "cold" with the 4 cm chamber agree very closely with the "hot" measurements with the 60 cm chamber.

Mr. Paton has kindly put at our disposal the full data which he obtained. These had never been worked up with care, as no reliable determination of the spectrometer constant was made, and the temperature of the grating was not recorded. The data are nevertheless valuable in several respects. Mr. Paton's "hot" curve was made at 250° C., with a chamber 6 cm long; thus the continuous spectrum in his curve is practically absent. We have computed wave-numbers from his data, using an arbitrary spectrometer constant to throw the wave-numbers into the right region, and have then subtracted the same parabola. Figure 2, III, is a smooth curve drawn through the points, the points themselves being omitted. It is clear that the law of spacing is still not a parabola.

The absorption-curves of a number of the lines in this set of data show a slight asymmetry which is suggestive of a satellite on the side of long wave-lengths. The degree of asymmetry lies within the experimental error of the determination of the absorption percentage, so it is not surprising that some lines should show an asymmetry on the other side. Of twenty-three lines in which the absorption percentage rises above 30 per cent, twelve lines show the asymmetry on the side of long wave-lengths, eight are symmetrical, two are irregular on both sides, and one shows the asymmetry on the other side. In Figure 3 are reproduced the absorption curves which show it most pronouncedly. The evidence is of course very slight. We had searched for the satellite, using a narrow slit-width, 0.25 mm, whereas most of our work has been done with a slit-width of 0.40 mm, and Imes and Paton used about 0.50 mm. We did not find the satellite. The galvanometer deflections were very small and the errors in absorption percentage correspondingly great, and it is possible, too, that the column of gas was too long and that the satellite, if it exists, was merged into the principal line.

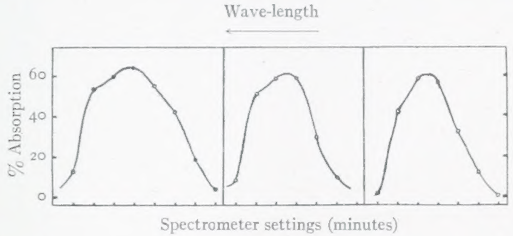

FIG. 3

The question has occasionally arisen whether accuracy in determinations of wave-numbers is to be gained by using a compensating chamber; that is, by observing galvanometer deflections first with the beam passing through the absorption chamber, and then with the beam passing through a chamber of equal length containing dried air. We did not use a compensating chamber in our work, but located absorption maxima directly from the curve of deflections. By way of comparison of the two methods, we have plotted from one of Mr. Paton's sets of data first the curve of deflections and then the curve of absorption percentage obtained from the deflections through the compensating chamber. The position of every absorption maximum on the two curves is practically identical.

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